Anion-Assisted Sigmatropic Rearrangements

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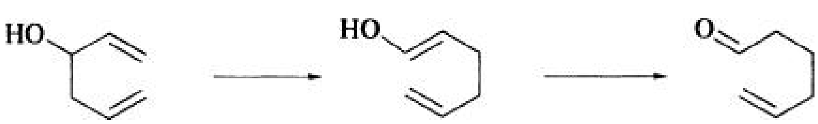
1. Introduction

The use of sigmatropic rearrangements for the synthesis of organic compounds has become one of the important synthetic tools available to the organic chemist, especially since the development of the detailed stereochemical understanding of these processes in terms of orbital symmetry. (1) The flexibility and predictability of the Cope rearrangement (Eq. 1) make this type of process widely applicable. (2) The

(1)

interest and synthetic activity related to the Cope rearrangement can be seen in a previous review of the Claisen and Cope rearrangements. (3) In that review, several variations of the rearrangement were discussed, including examples of the "oxy-Cope" rearrangement (Eq. 2). The name "oxy-Cope" rearrangement was first applied to the reaction shown in Eq. 3. (4) In 1975 examples of an oxy-Cope rearrangement were reported wherein an enormous rate acceleration (10^{15}) was observed on formation of the potassium salt of the oxy-Cope substrate (Eq. 4). (5)



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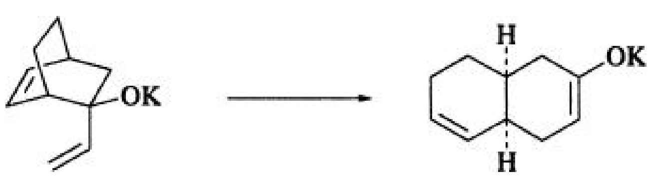

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This chapter surveys extensions of this type of anionic substituent effect to other [3,3]-, [5,5]-, [1,3]-, and [1,5]-sigmatropic rearrangements as well as retro-[2 + 2] and reverse Diels–Alder reactions. Specifically excluded are the ester enolate Claisen rearrangement which is mechanistically unrelated, (6) the Wittig rearrangement, (7) and the Haller–Bauer reaction. (8) The chemical literature has been searched to the end of 1989. Emphasis is placed on reactions of synthetic utility, novelty, and generality.

2. Mechanism and Stereochemistry

We now have a fairly clear picture of the anion-accelerated class of reactions. The anionic substituent is usually an alkoxide and must be placed on a carbon atom on the bond which is broken during the rearrangement. That bond is indicated by the dashed arrows in Eqs. 5–9b.

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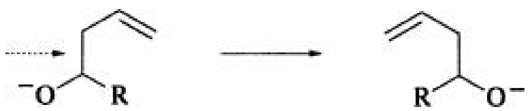


(6a)

(6b)

(7a)

(7b)

(7c)

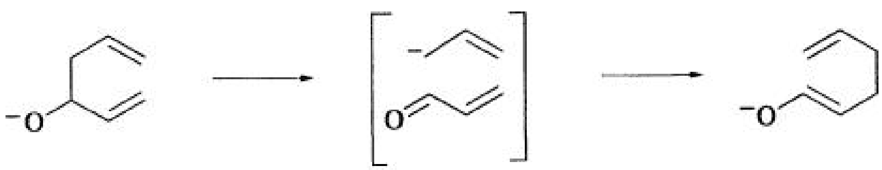
(8)

(9a)

(9b)

In each case, anion formation provides an electron “push” that assists carbon–carbon bond breaking. What simultaneous bond making may occur is not so important. (9) Examples are now known of [3,3]-sigmatropic rearrangements (Eq. 5), [1,3]-sigmatropic rearrangements (Eqs. 6a, 6b), cycloreversions (Eqs. 7a–7c), [1,5]-hydrogen shifts (Eq. 8), and electrocyclic ring openings (Eqs. 9a, 9b).

One can write a polarized transition state **1** for the oxy-Cope rearrangement that resembles an anion–carbonyl complex (Eq. 10). This formalism can be compared to the Lewis acid catalysis of the Diels–Alder reaction (Eq. 11) where stabilization of



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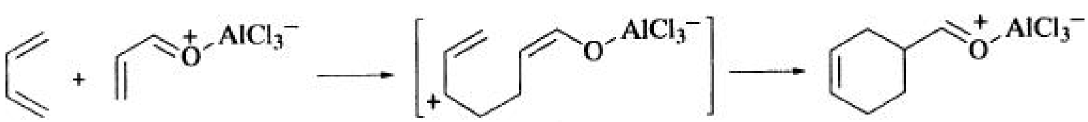

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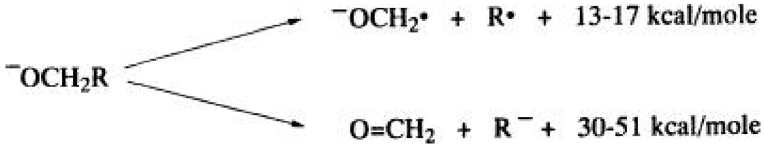
(11)

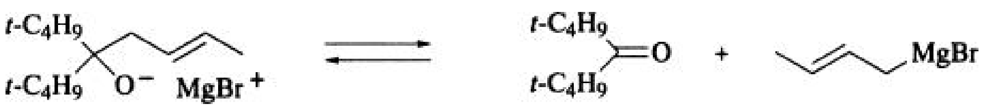
the bond-making step (intermediate **2**) is important. Thermodynamic estimation indicates that bond weakening by an alkoxide substituent provides 13-17 kcal/mol for bond homolysis; however, heterolysis is preferred over homolysis by an additional 17–34 kcal/mol (Eq. 12). (10, 11) Ab initio calculations confirm the dramatic effect of



(12)

the alkoxide substituent in weakening an adjacent bond. (12) These results are consistent with qualitative estimates of the effects of donor substituents. (13-16) The anionassisted oxy-Cope reaction has actually been observed in the gas phase in an ion cyclotron resonance spectrometer where ion-pairing or solvent effects are absent. (17)

The initial carbon–carbon bond cleavage resembles a reverse Grignard reaction. In a similar way, the initial adduct of di-*tert*-butyl ketone and 2-butenylmagnesium bromide reverts on standing (Eq. 13). (18) The very hindered alkoxide **3** fragments to produce di-*tert*-butyl ketone on formation of the potassium salt (Eq. 14). (19) The stability



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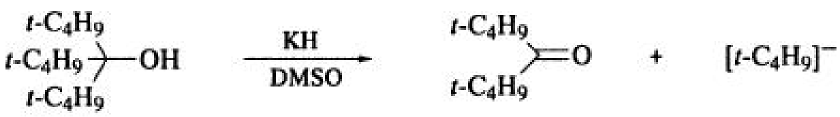

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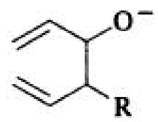
(14)

of the carbonyl group and the much higher basicity of a hindered alkoxide in polar aprotic solvents shifts the equilibrium from alkoxide to carbanion. Factors that make the alkoxide less stable (more basic), such as more polar solvents or the addition of complexing agents such as phase-transfer catalysts, (20-21a) will accelerate the reactions. Sterically crowded alkoxides, especially those derived from tertiary alcohols, are also likely to react faster. The effects of ion-pairing on fragmentation rates of alkali metal alkoxides has recently been examined. (21b) Besides the well-known order of dissociation (Cs > K > Na > Li), steric inhibition of ion-pairing and steric enhancement of reactivity have been quantified.

Sigmatropic rearrangements have been induced most commonly by an alkoxide substituent, although carbanions (Eq. 71) and amide anions (Eq. 156) have also been used. In addition, factors that stabilize the negative charge of the carbanion make the reactions go faster. Substituents on the diene **4** such as phenyl (Eq. 67), vinyl (Eq. 102), carboxy (Eq. 62), or aryl sulfide (Eq. 64) stabilize the developing negative charge and greatly accelerate the reaction.



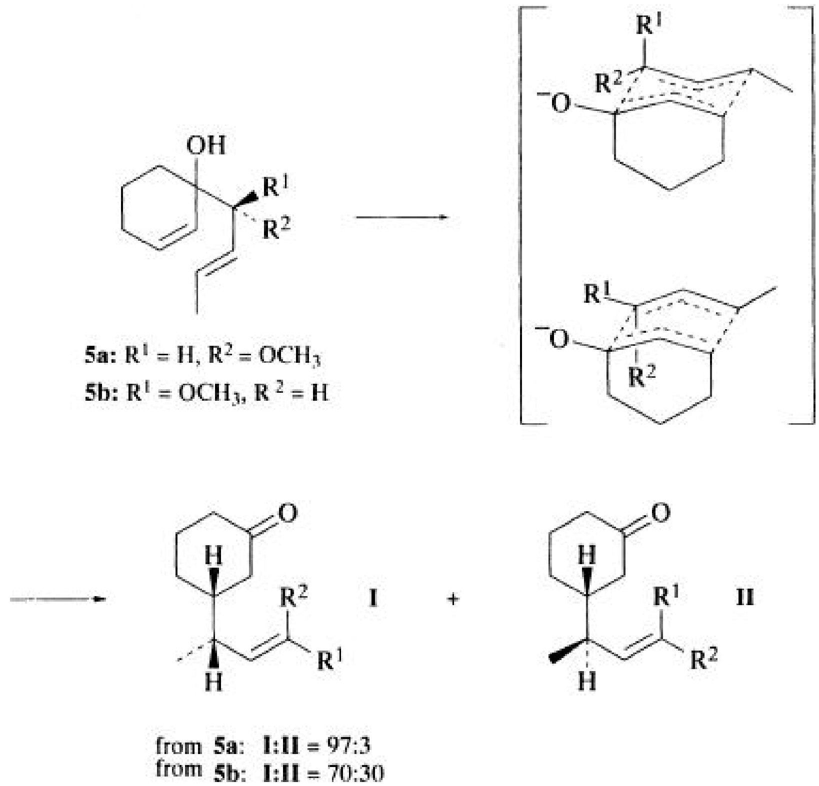
4: R = C_6H_5, CH=CH_2, CO_2H, SR^1

If the carbon–carbon bond being broken is intrinsically weak, as in cyclopropanes (Eq. 105) or cyclobutanes (Eq. 114), the isomerizations are generally very rapid.

Once the initial carbon–carbon bond breaking induced by the alkoxide substituent has begun, the product distribution and stereochemistry can often be predicted in terms of the known thermal rearrangements of substrates lacking the anionic substituent.

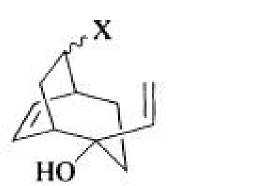
2.1. [3,3]-Sigmatropic Rearrangements

The Cope rearrangement usually occurs via a chair transition state. (3) The anion-assisted oxy-Cope often appears to be a concerted process that likewise proceeds via a chair transition state (Eq. 15). (22) The [3,3]-sigmatropic rearrangement of alkoxides



(15)

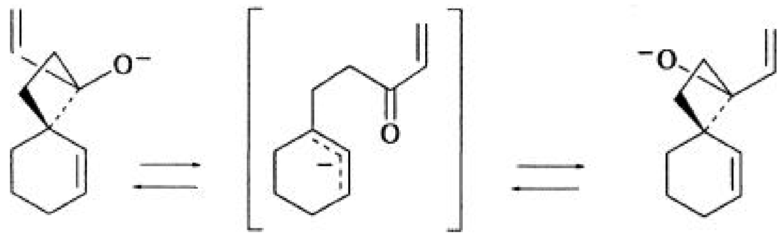
5a and **5b** occurs 97% via a chair transition state for **5a** and 77% for **5b**. Substrates that can only rearrange via the boat transition state will do so. A number of examples of 1,5-diene alkoxides such as **6** do not undergo rearrangement because the two ends of the diene cannot reach each other. (23) Typically in those cases competing [1,3] shifts or fragmentations are observed.



6: X = OC_4H_9-*n* or SC_4H_9-*n*

Sometimes epimerization can occur prior to rearrangement. Reaction of ketone **7** with vinylmagnesium bromide gives a mixture of epimeric alcohols that can be separated by chromatography (Eq. 16). (24) The potassium salts of both isomers undergo the anionic oxy-Cope rearrangement at room temperature, evidently via the equilibration shown in Eq. 17.

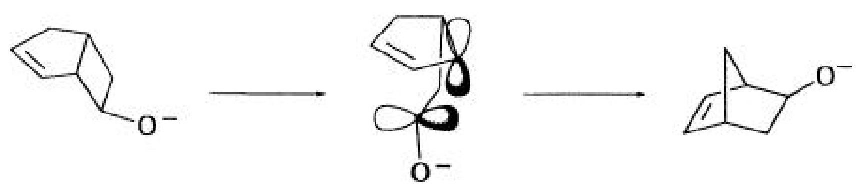
(16)



(17)

2.2. [1,3]-Sigmatropic Rearrangements

The stereochemistry of the [1,3] rearrangement is consistent with the Woodward–Hoffmann rules, that is, suprafacial carbon shift with inversion at the oxygen-bearing carbon (Eq. 18). (25) Another study with the isomeric cyclopropanols **8a** and **8b** (Eq. 19) confirms that the inversion pathway takes place when possible, but that stereospecific isomerization with retention at the migrating center also occurs. (26)



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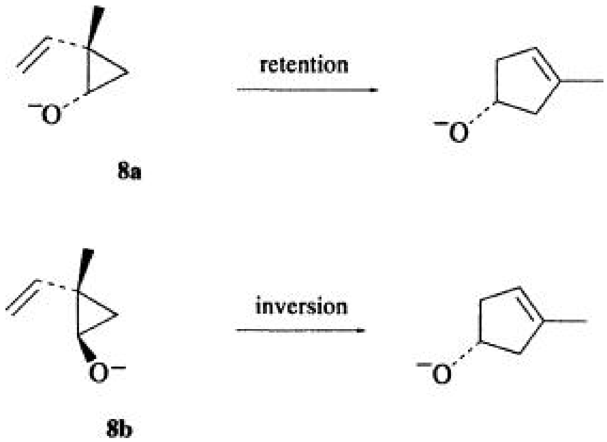
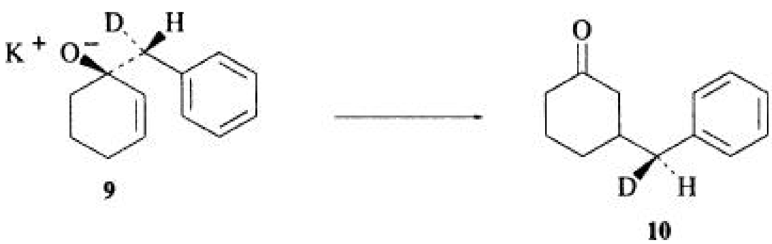


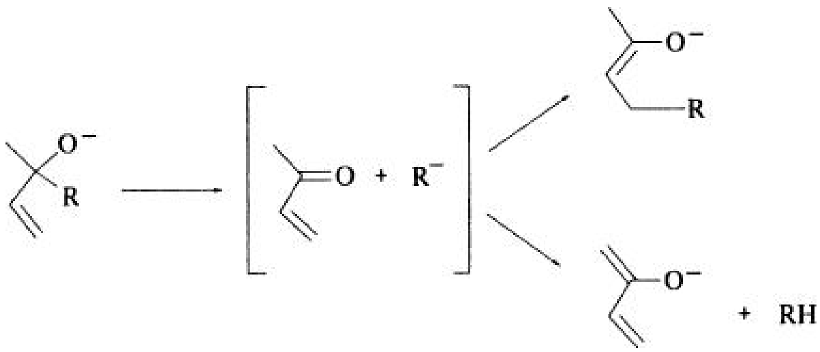
(19)

An elegant stereochemical study involves the [1,3]-sigmatropic shift of alcohol **9** to ketone **10** (Eq. 20). The isomerization proceeds with at least 65% retention at the



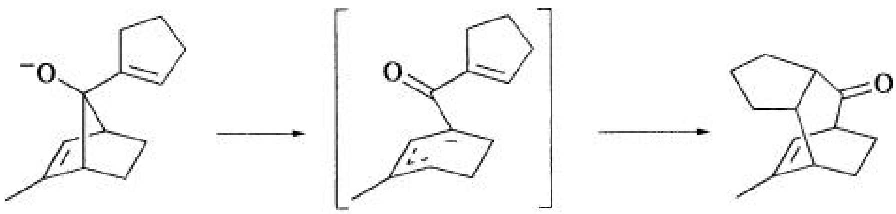
(20)

migrating center and not inversion, as predicted by orbital symmetry considerations. (27) This is consistent with the argument that an anionic substituent accelerates a forbidden pericyclic reaction more than it does an allowed one. (15) Although this general principle remains to be proven, it is true that in many [1,3]-sigmatropic shifts rearrangement occurs via the “forbidden” suprafacial–retention mechanism. The reaction is about 75% intramolecular. The evidence that at least some product is derived by an intermolecular pathway is consistent with the notion that a highly polarized transition state is involved (Eq. 21). In most of the anion-assisted rearrangements



(21)

to be described, such a transition state sometimes leads to fragmentation as a major side reaction, a proton being abstracted either from solvent or from the ketone intermediate. The anion-assisted [1,3]-sigmatropic rearrangement of **11** cannot be concerted (Eq. 22); it probably proceeds via allyl anion **12**. (28)



11 12

(22)

2.3. Cycloreversions

The anion-assisted [2 + 2] cycloreversion of *cis*-2,3-dimethylcyclobutanol is not completely stereospecific, although the expected *cis* olefin is the major product (Eq. 23). (29) There has been no stereochemical study of the related [4 + 2]-cycloreversion reaction.

52 : 30 : 18

(23)

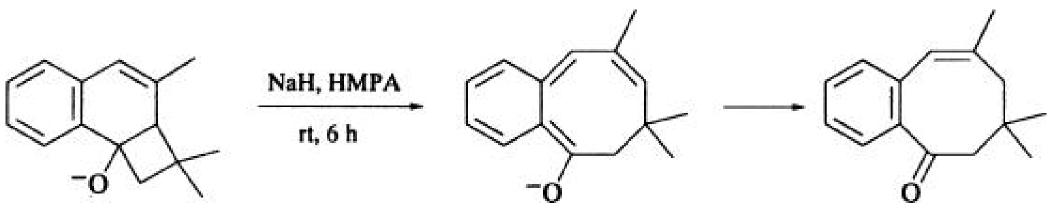
2.4. [1,5]-Sigmatropic Shifts

The few examples of anion-assisted [1,5]-hydrogen shifts (e.g., Eq. 24) occur in medium-sized rings where the propensity for transannular hydrogen migrations is well known. (30) There are no examples where the expected suprafacial stereochemistry has been established.

(24)

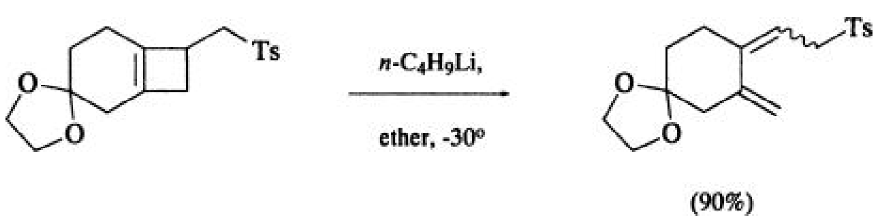
2.5. Electrocyclic Ring-Opening Reactions

The anion-assisted [4 π + 2 σ] electrocyclic ring opening (Eq. 9a) is not well represented. The single example (Eq. 25) could also be written as a direct fragmentation reaction, and no stereochemical information is available. (31)



(25)

The anion-assisted [2 π + 2 σ] electrocyclic ring-opening reaction (Eq. 26) generally produces mixtures of isomers, but it is not known whether they correspond to conrotatory or disrotatory ring opening. (32a)



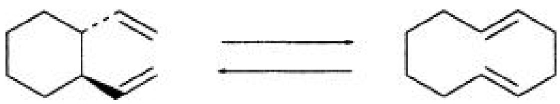
(26)

3. Scope and Limitations

3.1. [3,3]-Sigmatropic Rearrangements

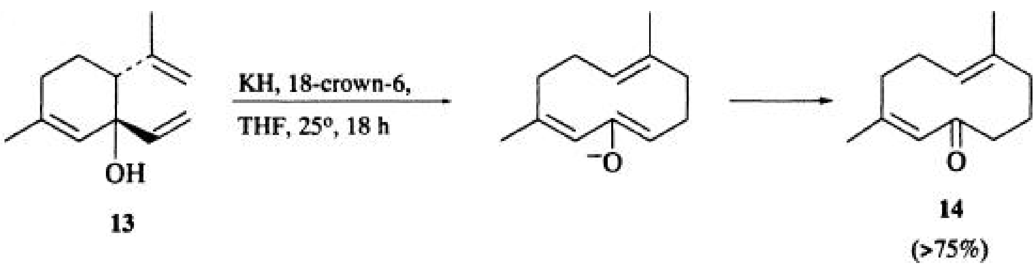
3.1.1.1. 1,2-Divinylcycloalkanols

Ring expansion of 1,2-divinylcycloalkanols by anion-assisted [3,3]-sigmatropic rearrangement is a useful route to previously difficultly accessible 1,5-cyclodecadienes. 32b,32c,33–38 Normally the divinylcyclohexane–cyclodecadiene Cope rearrangement (Eq. 27) is reversible and lies heavily on the



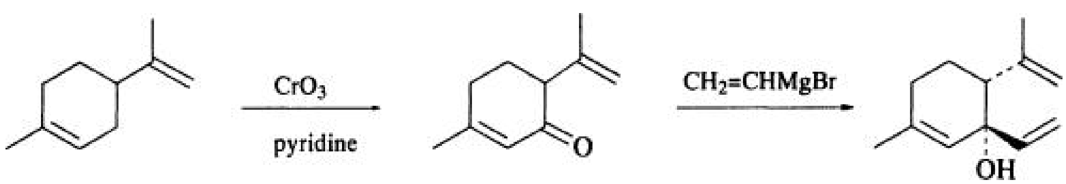
(27)

side of the 1,2-divinylcyclohexane. Formation of the potassium salt of alcohol **13** in the presence of 18-crown-6 in tetrahydrofuran (THF) leads to the production of ketone **14** in greater than 75% yield after 18 hours at room temperature (Eq. 28). (34)



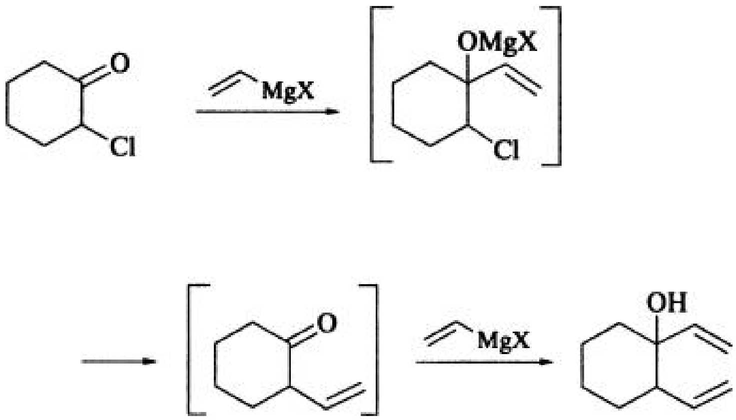
(28)

Preparation of divinylcycloalkanols can be accomplished in a number of ways. Some α -vinylcyclohexanones are available from related terpenes (Eq. 29). (33, 34, 38) Addition of vinylmagnesium bromide then affords the requisite divinylcycloalkanols. (34)



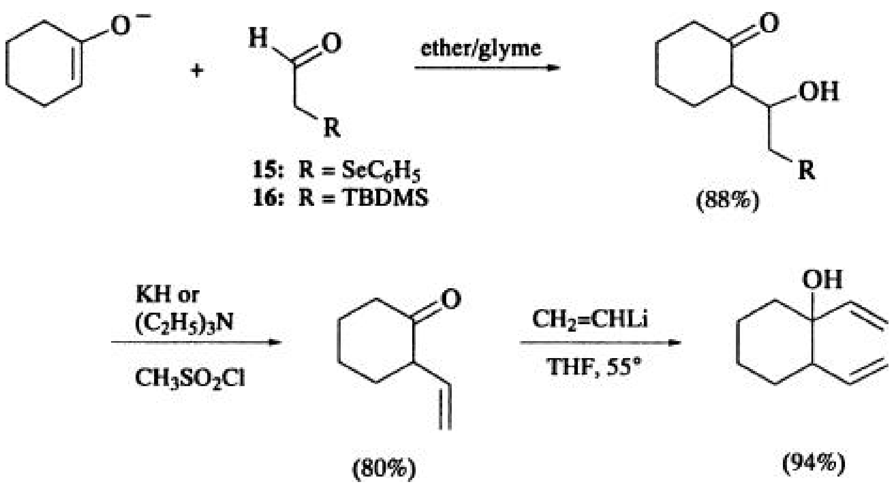
(29)

Methods have also been developed for producing divinylcycloalkanols in one step from α -chloroketones via addition–rearrangement reactions (Eq. 30). (39) A variation involves the addition of alkynyl Grignard reagents to α -chloroketones followed by reduction–rearrangement with lithium aluminum hydride. (40)



(30)

Other approaches use either aldehydes **15** (32b-37) or **16** (41) for direct vinylation of ketones (Eq. 31). Photocycloaddition of allene to cyclohexenone and other special routes to divinylcarbinols can also be employed (Eq. 32). (32c-36)



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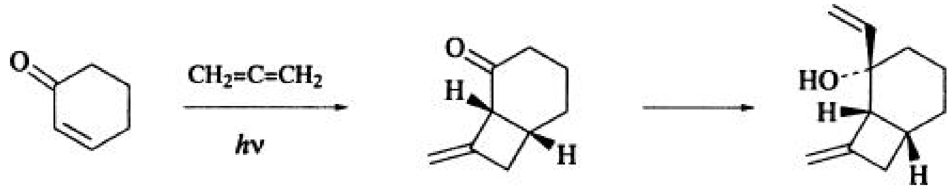
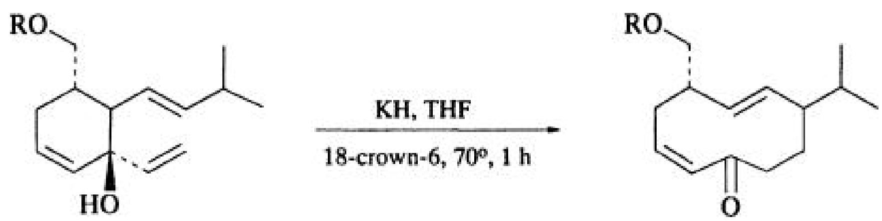


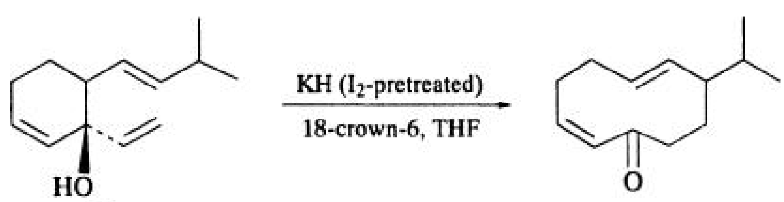
(32)

Divinylcyclohexanols generally rearrange as the potassium salts in tetrahydrofuran at room temperature or at reflux. The salts are most often formed by treatment of the corresponding alcohols with a slight excess (usually 1.2 equivalents) of potassium hydride. For example, alcohol **17** rearranges in tetrahydrofuran when treated with potassium hydride and 18-crown-6 at reflux for 1 hour (Eq. 33). (36) A related alcohol is deprotonated and rearranged using five molar equivalents of potassium hexamethyldisilazide [KN(TMS)$_2$]. (38)



(33)

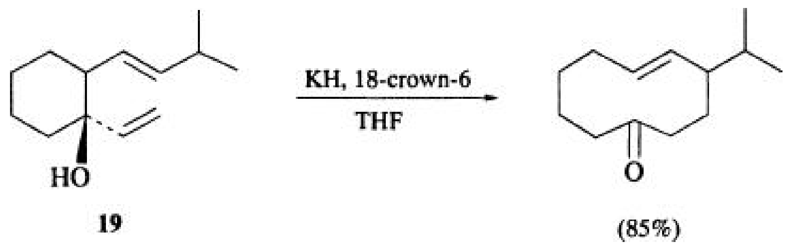
Because of the importance of this approach to the germacrane sesquiterpenes, considerable efforts to optimize conditions for the rearrangement have been reported. The [3,3]-sigmatropic rearrangement of alcohol **18** (Eq. 34) is extremely sensitive to batches of potassium hydride from different commercial sources. In contrast, the alcohol **19** always rearranges smoothly (Eq. 35). Purification of potassium hydride by pretreatment with iodine (this process converts contaminating elemental potassium or potassium superoxide into potassium iodide) leads to reproducibly high yields in the reactions of both Eq. 34 and Eq. 35. (42)



18

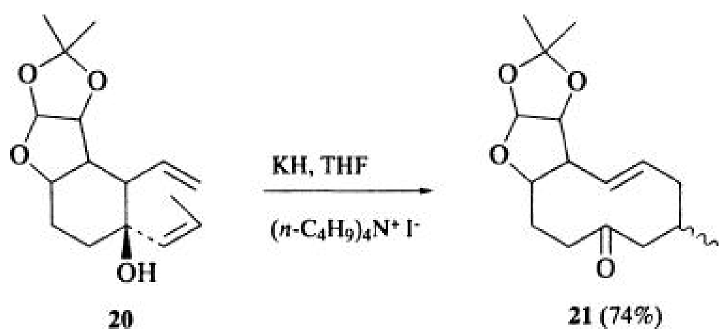
(70-80%)

(34)



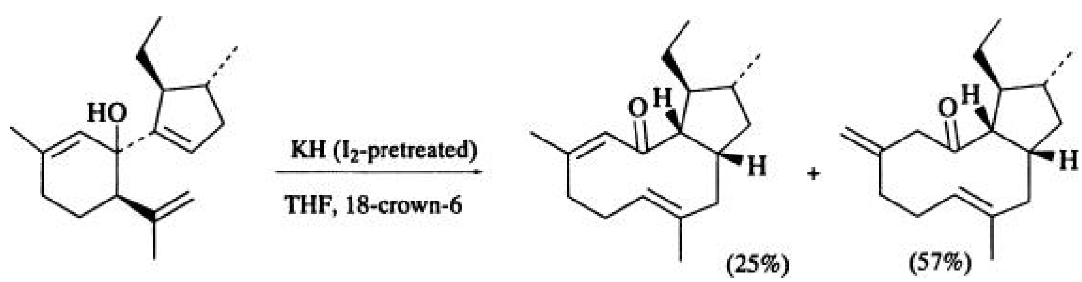
(35)

Treatment of alcohol **20** with potassium hydride under the usual conditions leads only to decomposition. (20) If a catalytic amount of tetra-*n*-butylammonium iodide, a phase transfer catalyst known (20) to enhance the alkylation of potassium alkoxides, is



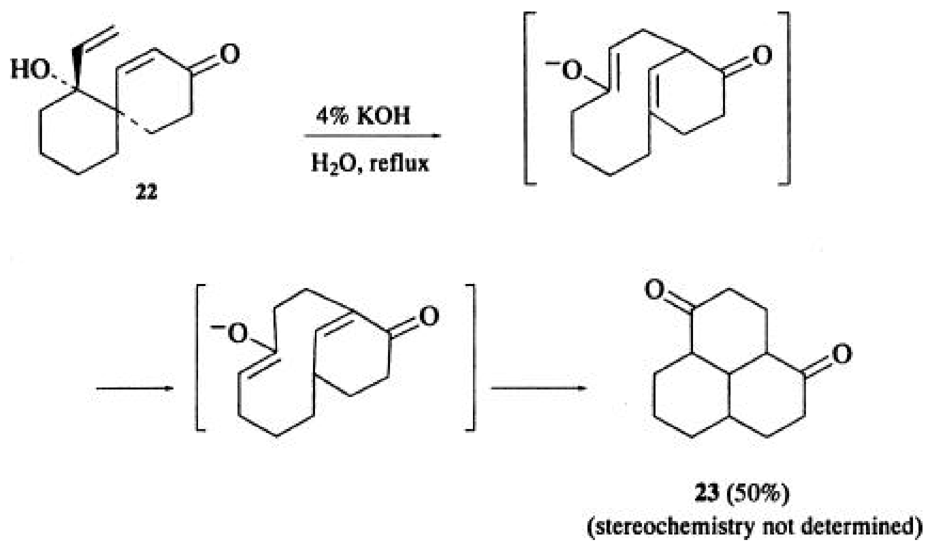
added, the [3,3]-sigmatropic rearrangement proceeds smoothly to produce ketone **21** in 74% yield. This is the only report of such a salt effect. It is likely that other types of isomerizations can be enhanced by this technique as well.

An extensive study of chirality transfer in the [3,3]-sigmatropic shift (Eq. 36) affirms that rearrangement occurs via a chair transition state. (43)



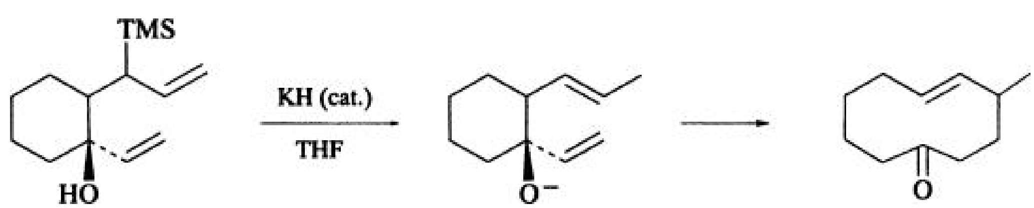
(36)

Several rearrangements of divinylcarbinols are followed by further condensation of the resulting enolates. (44-47) For example, hydroxy ketone **22** is converted into diketone **23** via rearrangement followed by transannular cyclization (Eq. 37). Very mild basic conditions suffice in this reaction because the carbanion-stabilizing ketone group in 22 allows the critical bond-breaking step to occur without a completely free alkoxide. (44)



(37)

An interesting example of the in situ generation of a divinyl precursor by desilylation is shown in Eq. 38. (48)



(38)

Application of the divinylcyclohexane oxy-Cope rearrangement to the total synthesis of periplanone B (49, 50) and 13-norheliangolides (51) has been reported.

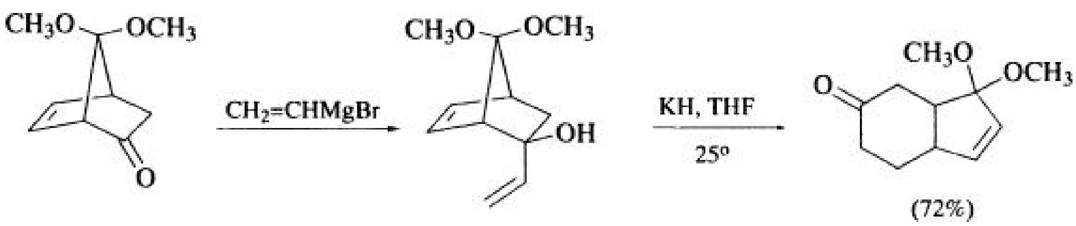
3.1.1.2. Bicyclic Vinylcarbinols

The rearrangement of bridged vinylcarbinols such as **24** (Eq. 39) leads to 5/6, 6/6, and 7/6 fused ring systems. (5, 23, 52, 53) The strain in

24: n = 1,2,3 m = 1,2

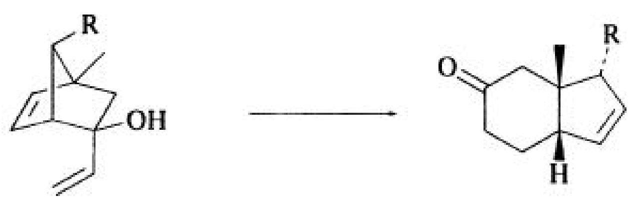
(39)

bicyclo[2.2.1]heptenes and bicyclo[2.2.2]octenes accelerates these reactions. Thus treatment of 7,7-dimethoxybicyclo[2.2.1]hept-4-en-1-one with vinylmagnesium bromide followed by potassium hydride leads to the rearrangement product in 72% yield (Eq. 40). (54, 55) On the other hand, 7-vinylbicyclo[2.2.1]heptenes usually undergo [1,3]-sigmatropic rearrangements instead (28) because geometric constraints prevent them from achieving the proper transition state for the [3,3] rearrangement.



(40)

Isomerization of alcohol **25a** to the corresponding bicyclic compound **26a** with potassium hydride in tetrahydrofuran occurs through the dianion (Eq. 41). When the

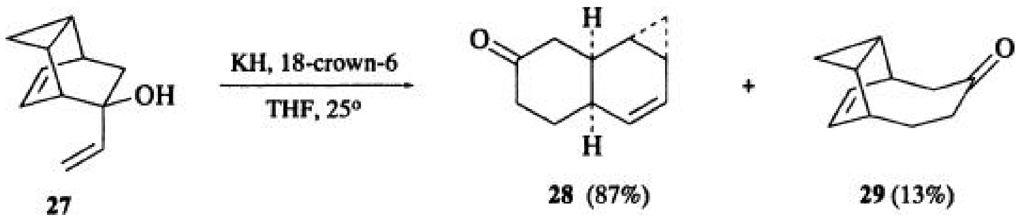


25a: R = CH_2OH
25b: R = $CH(OCH_3)_2$
25c: R = $OCH_2C_6H_5$

26

(41)

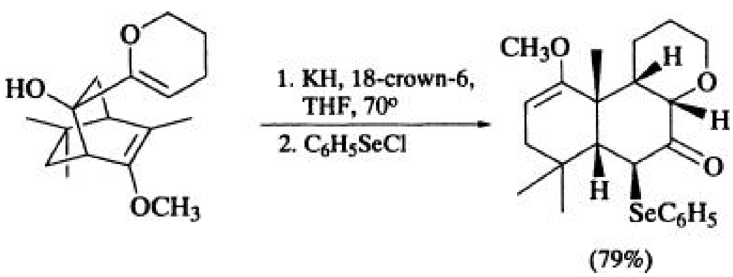
potassium or sodium salt of acetal **25b** is heated in tetrahydrofuran, no reaction occurs. However, the sodium salt of **25b** isomerizes to **26** on heating in benzene. (56a) This unusual result contrasts with the typical rate enhancements observed in polar aprotic (and ionizing) solvents. It is possible that the *syn* disposition of the acetal group in **25b** promotes coordination with the alkoxide, thus reversing the typical solvent effect. Isomerization of benzyl ether **25c** to the analogous bicyclo[4.3.0]ketone **26c** is used in the synthesis of steroidal C/D units. (56b) Entry into the aristolane family of sesquiterpenes is achieved by [3,3]-sigmatropic rearrangement of alcohol **27** to give the expected Cope product **28** as well as small amounts of compound **29**, derived via a competing [1,3] shift (Eq. 42; see later section and Table VIII.) (57) This side reaction is not observed when the rearrangement is carried out without 18-crown-6.



27

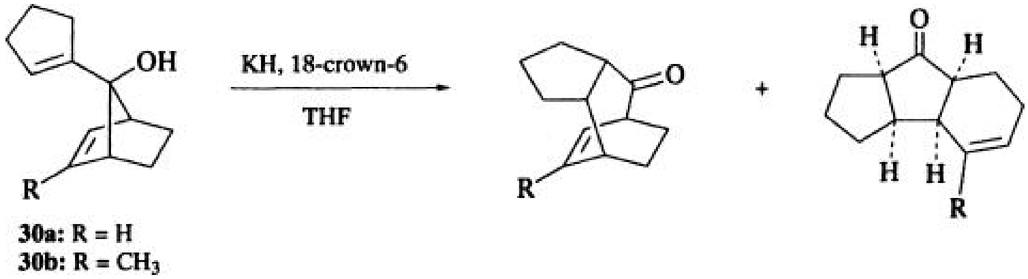
(42)

Construction of the forskolin skeleton by anion-assisted oxy-Cope rearrangement is shown in Eq. 43. (58) This reaction has also been used in the total synthesis of reserpine (59) and dihydroneptalactone, (60) and in the synthesis of a structure that had been assigned to cannivonine. (61)

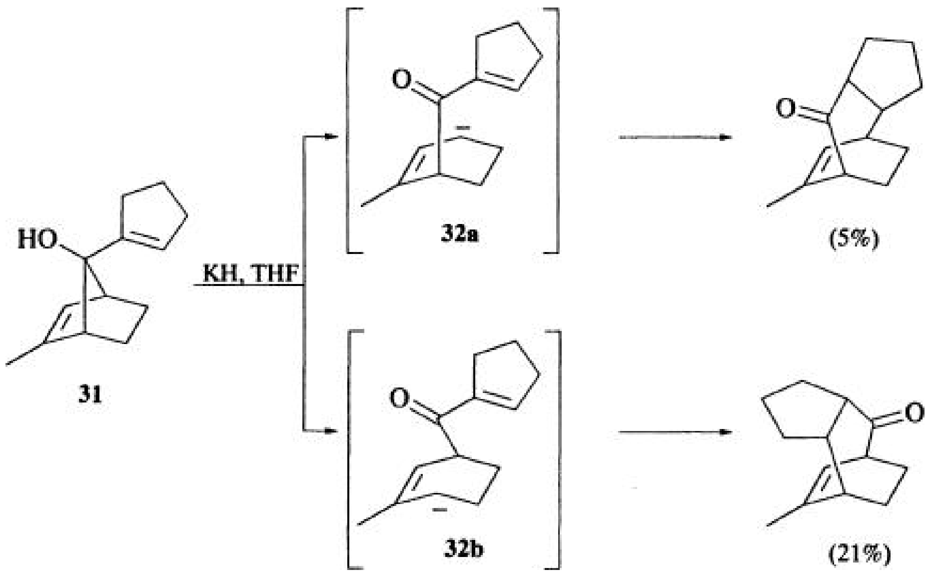


(43)

Base treatment of alcohols **30a** or **30b** leads to products of both [1,3] and [3,3] rearrangements (Eq. 44). (28) Rearrangement of the isomeric alcohol **31** cannot be concerted; it proceeds instead by way of allyl anions **32a** and **32b** (Eq. 45). The latter is favored since the electron-donating methyl substituent is on the center atom of the allyl anion.

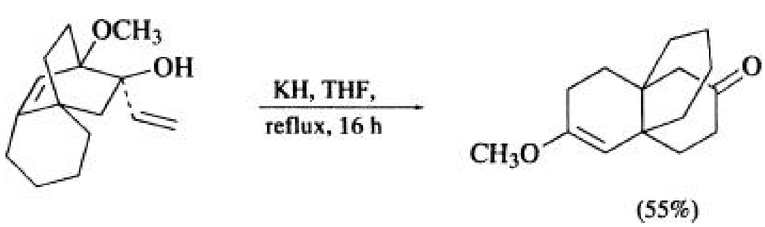


(44)

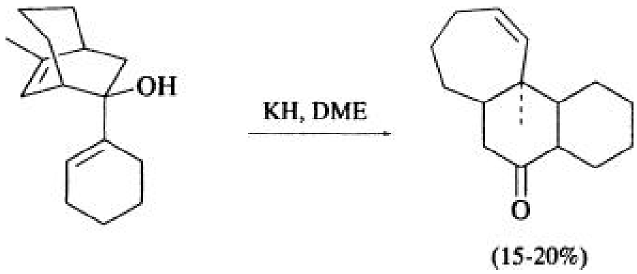


(45)

Incorporation of additional rings into the substrates leads to propellanes (Eq. 46) (62) or tricyclic systems (Eq. 47). (53)

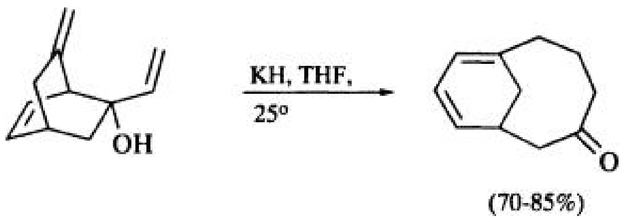


(46)

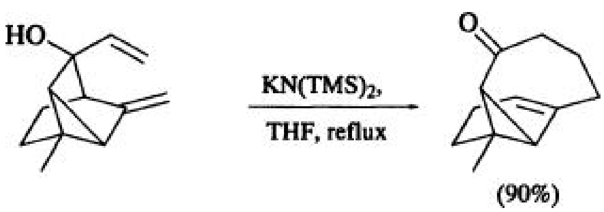


(47)

Bicyclic allylic alcohols with an exocyclic double bond rearrange to bridged bicyclic ring systems (Eq. 48). (52) This type of reorganization leads to the ring system of the natural product cerorubenic acid III (Eq. 49). (63)



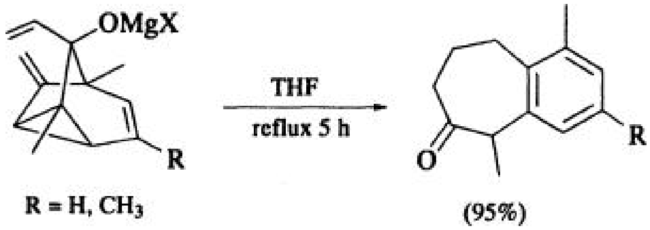
(48)



(49)

Two final examples of anionic oxy-Cope rearrangements in bicyclic systems are shown in Eqs. 50 (64) and 51. (65) These deep-seated rearrangements are believed to occur via an initial [3,3]-sigmatropic reaction.

(50)



(51)

3.1.1.3. Allylcycloalkenols

Alcohols of type **33**, which are obtained by 1,2 addition of allylic organometallics to cyclohexen-3-one, undergo the alkoxide-assisted Cope rearrangement to give ketones which are the formal 1,4 adducts of the original cyclic enone (Eq. 52).

33

(52)

The stereochemistry of this reaction has been studied extensively (Eq. 53). (22) The conditions are rather vigorous, requiring heating the potassium salt at 110° in diglyme for 38 hours. The reaction leads to side products from solvent decomposition when carried out in hexamethylphosphoric triamide. The reaction in Eq. 53 has been carried out with potassium hydride in diethylene glycol dimethyl ether at 70° in the presence of 18-crown-6 with slight changes in the *trans/cis* ratios.

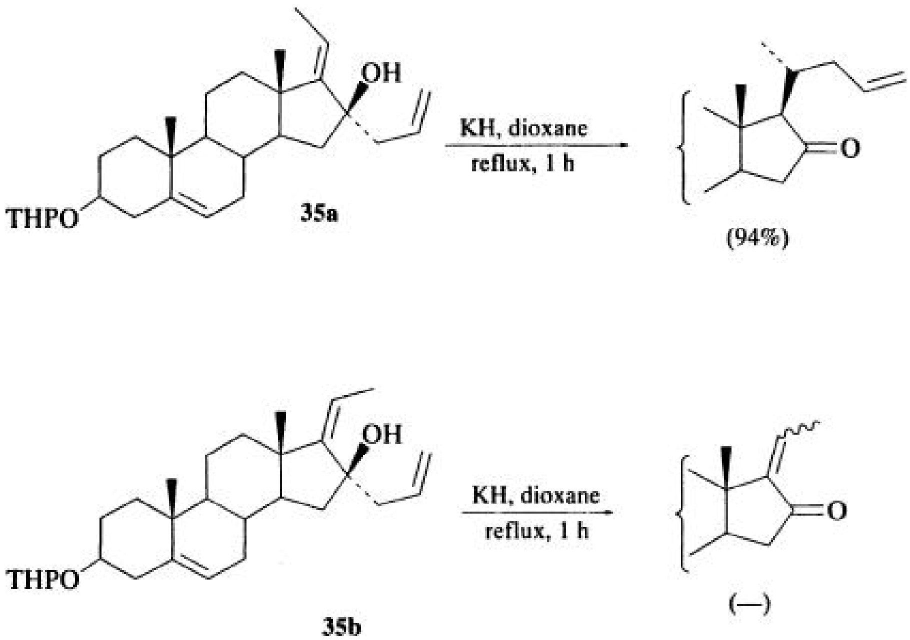
(53)

$R^1 = H$; $R^2 = OCH_3$ **34** (77%)

$R^2 = OCH_3$; $R^2 = H$ (96%)

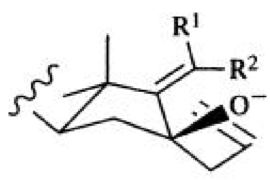
This rearrangement can also be used to construct steroid side chains (Eq. 54);

([66]) heating the potassium salt of **35a** in dioxane at 100° is required to effect rearrangement.



(54)

The *Z* isomer **35b** does not rearrange but cleaves under the same conditions, owing to a congested transition state **36** (R^1 = H, R^2 = CH_3) with an unfavorable quasi-1,3-diaxial interaction of the C-21 methyl group with the alkoxide.

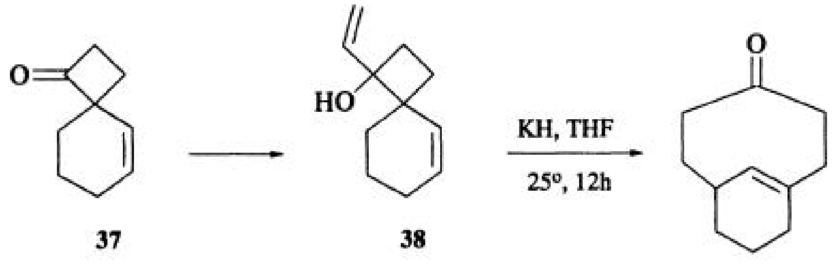


36

A number of examples of fragmentation of homoallylic alcohols are known. ([67]) This side-chain reaction is discussed in more detail in the sections on fragmentation and common side reactions.

3.1.1.4. 1,2-Divinylcyclobutanols

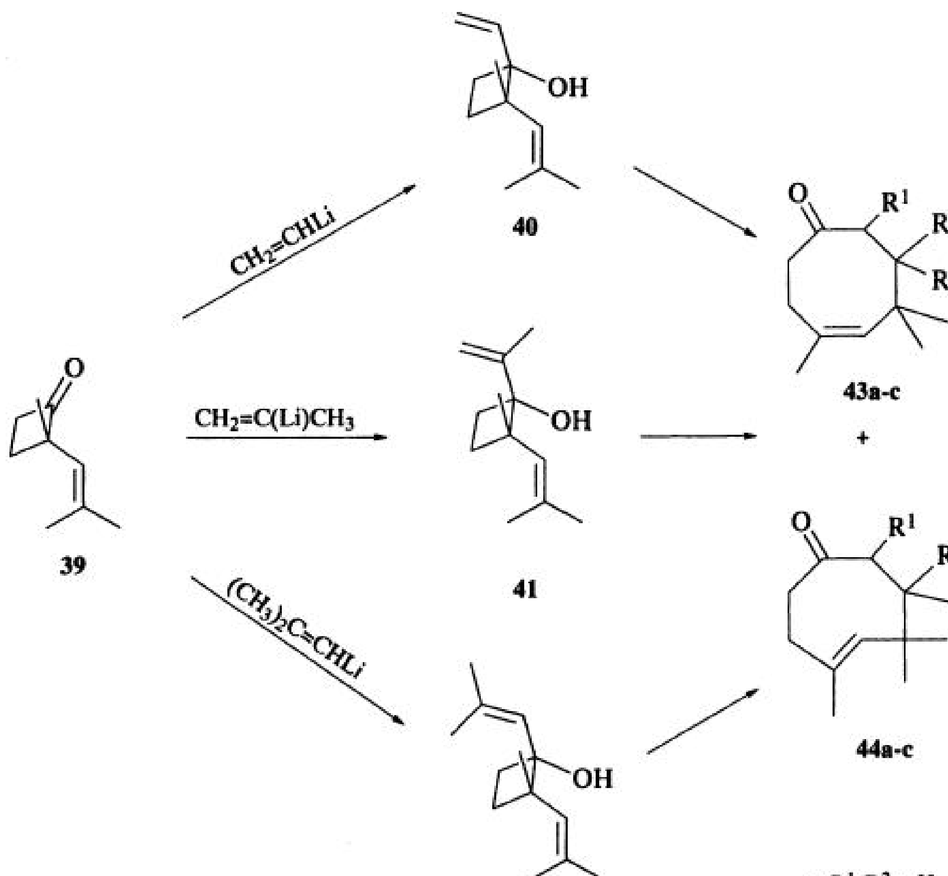
Cyclobutanones such as **37** are readily available by spiroannulation of 2-cyclohexen-1-one with 1-lithiocyclopropyl phenyl sulfide. ([68]) Reaction of ketone **37** with vinylmagnesium bromide gives a mixture of epimeric alcohols **38** that can be separated by chromatography. The potassium salts of both isomers undergo the anionic oxy-Cope rearrangement at room temperature (Eq. 55; see also Eq. 17). (24, 35, 69)



37 38 (80%)

(55)

Ketone **39** reacts with vinyllithium, isopropenyllithium, or isobutenyllithium to produce alcohols **40**, **41**, or **42**, respectively (Eq. 56). Treatment of alcohol **40** with



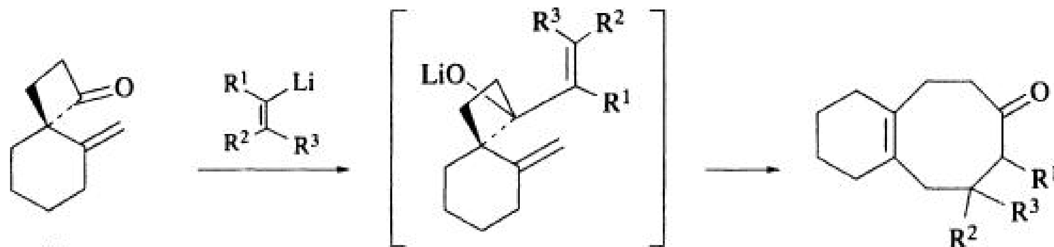
39 40 41 42 43a-c 44a-c

(56)

a: R^1-R^3 = H
b: R^1 = CH_3; R^2,R^3 = H
c: R^1 = H; R^2,R^3 = CH_3

potassium hydride in tetrahydrofuran leads to rapid formation of the *cis*- and *trans*-cyclooctenones **43a** and **44a** in a ratio of 79:21 in 62% yield. Similar treatment of alcohol **42** gives ketones **43c** and **44c** in a ratio of 67:33 in 49% yield. Alcohol **41**, on the other hand, gives ketone **44b** exclusively in 50% yield. (24) The different product ratios can be rationalized on the basis of steric effects in the chair- and boat-like transition states. Since the two olefinic groups are 95% *trans* to each other in all three alcohols, *cis/trans* interconversion must be rapid (cf. Eq. 17).

Ring expansion occurs easily when alkenyllithiums react with ketone **45** (Eq. 57). (24) Relief of ring strain and probably ideal overlap of the exocyclic double

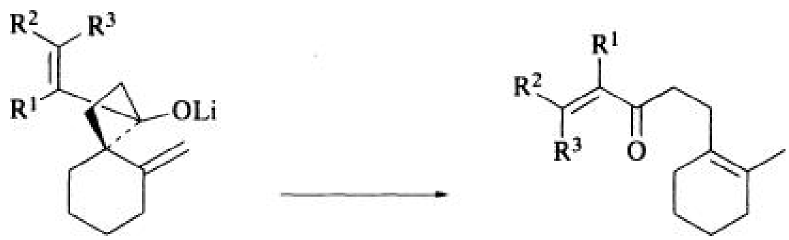


45

(57)

a: $R^1 - R^3 = H$
b: $R^1 = CH_3$; $R^2, R^3 = H$
c: $R^1, R^2 = CH_3$, $R^3 = H$

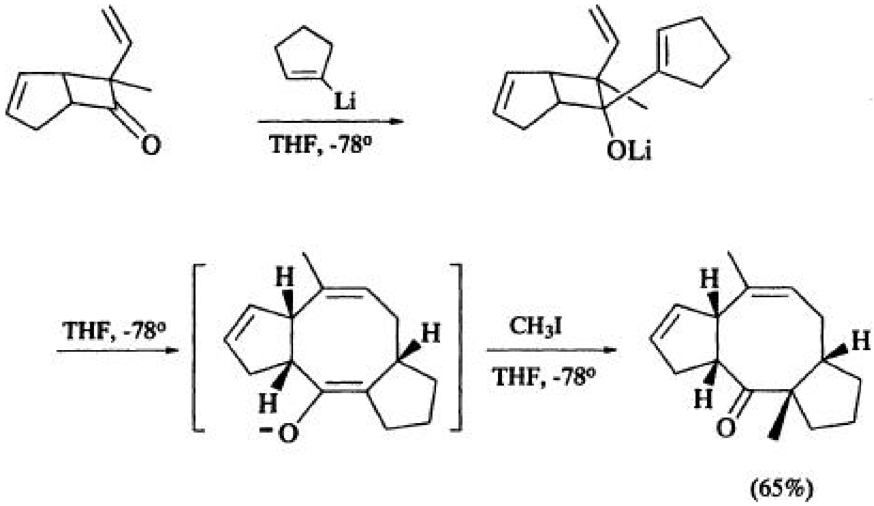
bond with the cleaving bond make isolation of the alcohols prior to rearrangement difficult. The *trans* divinyl isomers in this case give cleavage products (Eq. 58).



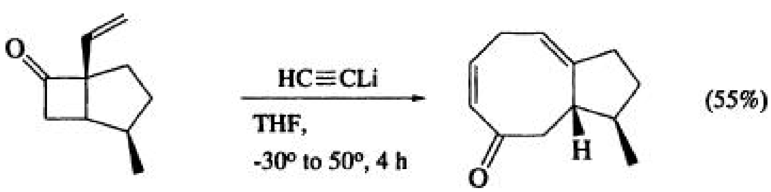
(58)

An application of the anion-assisted divinylcyclobutanol oxy-Cope rearrangement to the synthesis of the ophiobolin skeleton (Eq. 59) indicates that the strain inherent in the four-membered ring allows the rearrangement of the lithium salt to proceed at low temperature. The tricyclic ketone is isolated in 65% yield after quenching at –78° with methyl iodide to alkylate the enolate formed in the rearrangement. 70a,70b

Application to the total synthesis of the sesquiterpenes poitediol and 4-epipoitediol involves an acetylenic variant of this process (Eq. 60). (70c)



(59)



(60)

3.1.1.5. Open-Chain Systems

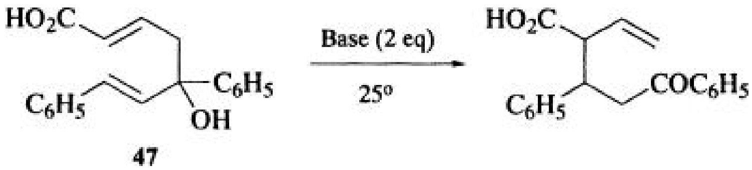
The few acyclic examples of anion-assisted oxy-Cope rearrangements allow a comparison of substituent effects and reaction conditions. For example, rearrangement of the simple substrates **46a** and **46b** (Eq. 61) (71) requires

46a: $R^1 = CH_3$; $R^2 = H$
46b: $R^1 = C_2H_5$; $R^2 = H$
46c: $R^1 = SC_6H_5$; $R^2 = H$
46d: $R^1 = CH{=}CH_2$; $R^2 = CH_3$

(61)

heating the potassium salt to 85° in dimethoxyethane. Reaction of the phenylthio derivative **46c**, however, proceeds smoothly at room temperature in tetrahydrofuran because of the anion-stabilizing ability of the sulfur atom. (10) Similarly, the vinyl-substituted compound **46d** rearranges as the zinc salt in tetrahydrofuran. (72) The double bond also promotes bond breaking in the transition state and thus accelerates the reaction. Both *threo* and *erythro* isomers of substrates **46a** and **46b** show 67–95% *E* selectivity. (73) Some of these results have been reviewed. (74)

Isomerization of the hydroxy acid **47** in the presence of an unspecified base proceeds under very mild conditions (Eq. 62). (75a)

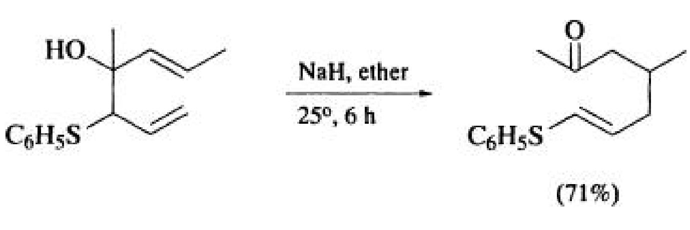


(62)

A number of other examples involve the isomerization of methoxy-substituted substrates (Eq. 63). These reactions, in contrast to those in Eq. 61, require rather vigorous conditions. The potassium salts must be heated to 85° in dimethoxyethane to effect rearrangement.

(63)

Cleavage side reactions can be suppressed by decreasing the ionic character of the metal alkoxide bond. For example, the rearrangement in Eq. 64 proceeds normally

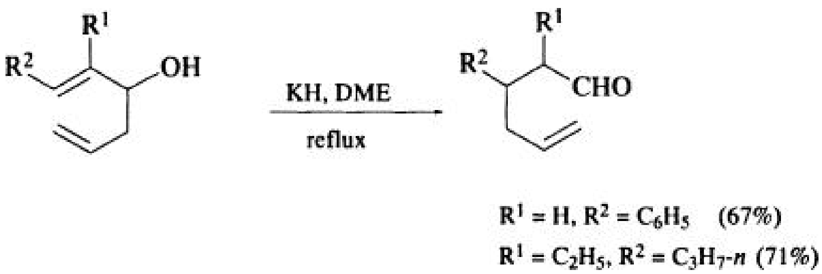


(64)

in diethyl ether in 71% yield, but the same reaction in tetrahydrofuran, which favors ionization, leads to cleavage. (75b) An extensive study of examples of the acyclic oxy-Cope process in a series also prone to cleavage has delineated some of the factors (such as steric congestion around the forming C

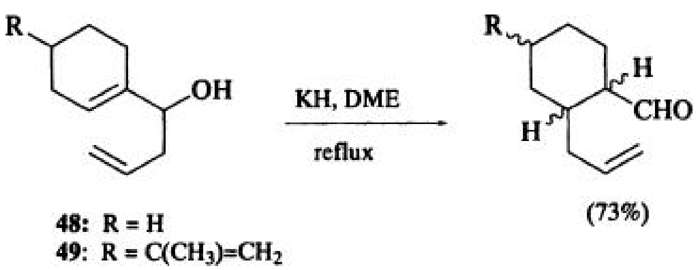
- C bond) that promote cleavage. (76) These factors are discussed in the section on side reactions.

When a 3-hydroxy-1,5-hexadiene is substituted on C-1 and C-2, the 1,2-disubstituted 5-hexenal is generally produced in good yield (Eq. 65). (77) Application to compounds



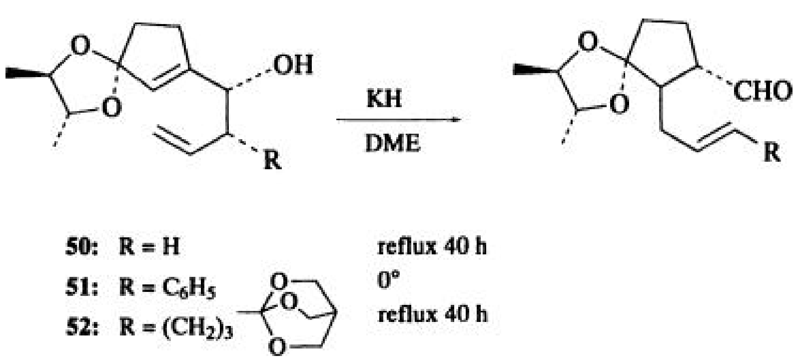
(65)

where R^1 and R^2 represent a ring are particularly useful. When a ring substituent is present, as in compound **49**, mixtures of diastereomers are obtained (Eq. 66). (78)



(66)

Equation 67 illustrates the application of such an anion-assisted oxy-Cope rearrangement to prostaglandin synthesis. (79) The potassium salts of alcohols **50** and **52**

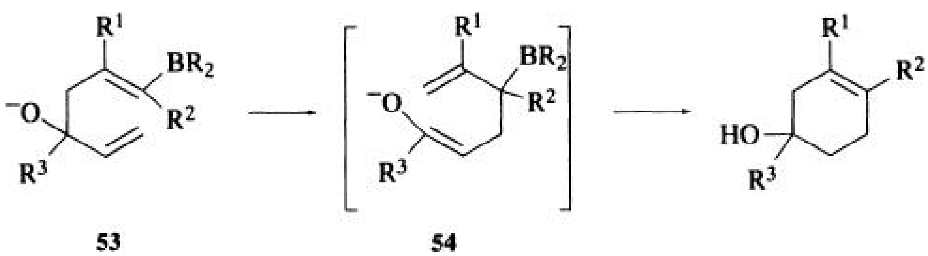


(67)

rearrange in dimethoxyethane at reflux and give the products in 56 and 58% diastereomeric excess. On the other hand, compound **51** rearranges at 0° with 0% diastereomeric excess. The identical diastereofacial selectivity observed when R = H and R = alkyl implies that the anion-assisted rearrangement must proceed in both cases via an axial alkoxide (Eq. 68). The rate enhancement by the phenyl substituent is to be expected since it is an anion-stabilizing group; the lack of diastereofacial selectivity observed is thus attributed to a change in mechanism to a stepwise process.

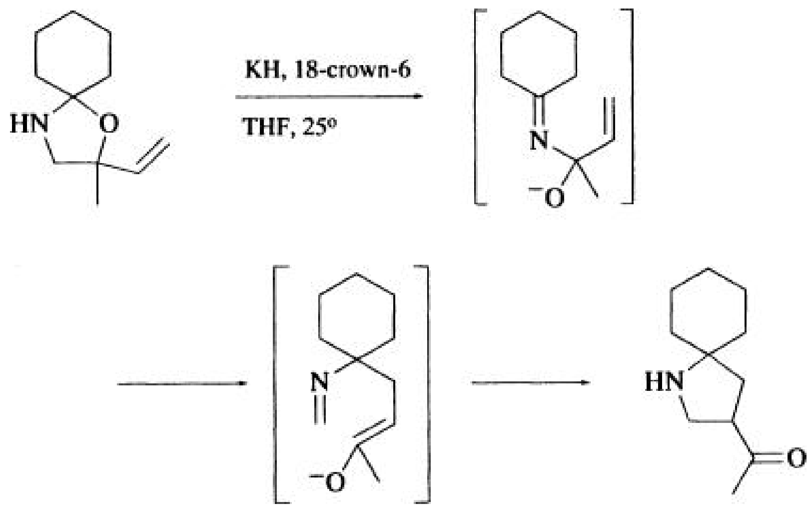
(68)

The anion-assisted rearrangement of borane **53** is followed by an interesting ring closure of the intermediate allylborane **54** (Eq. 69). (80) The mechanism of the second step is unknown.



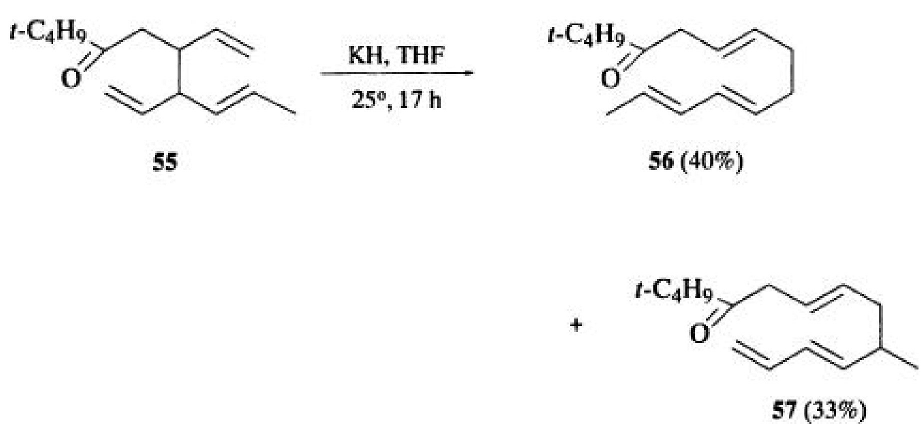
(69)

Equation 70 illustrates a reaction that may proceed by an anion-assisted [3,3]-sigmatropic rearrangement involving a nitrogen–carbon double bond. Several examples of this type of rearrangement are known. (81)



(70)

An example of a carbanion-accelerated [3,3]-sigmatropic rearrangement is shown in Eq. 71. (82) The potassium enolate of ketone **55** isomerizes via a Cope process to approximately equal amounts of isomers **56** and **57**. There are many examples of [1,3]-sigmatropic shifts, (83) reverse [2 + 2] cycloadditions, and electrocyclic [2 π + 2 σ] cycloreversions that are accelerated by carbanions.

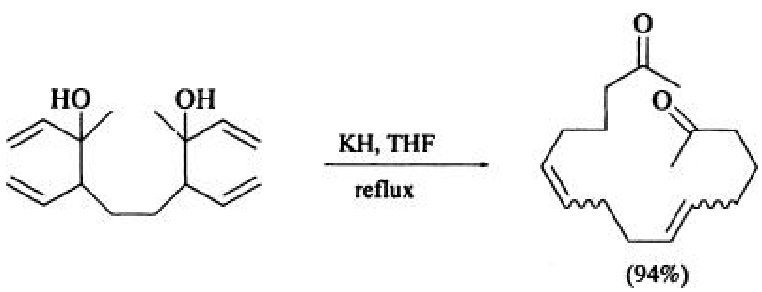


(71)

Cleavage of the trimethylsilyl ether **58** by fluoride ion does not result in a subsequent [3,3]-sigmatropic rearrangement (Eq. 72). (84) On the other hand, the in situ cleavage of a trimethylsilyl ether by potassium hydride (presumably containing trace amounts of potassium hydroxide) is known to result in a [3,3]-sigmatropic rearrangement. (48) A successful fluoride ion induced anion-assisted retro Diels–Alder reaction is shown in Eq. 151.

(72)

The single example of a double anion-assisted oxy-Cope rearrangement is used in a total synthesis of muscone (Eq. 73). (85)



(73)

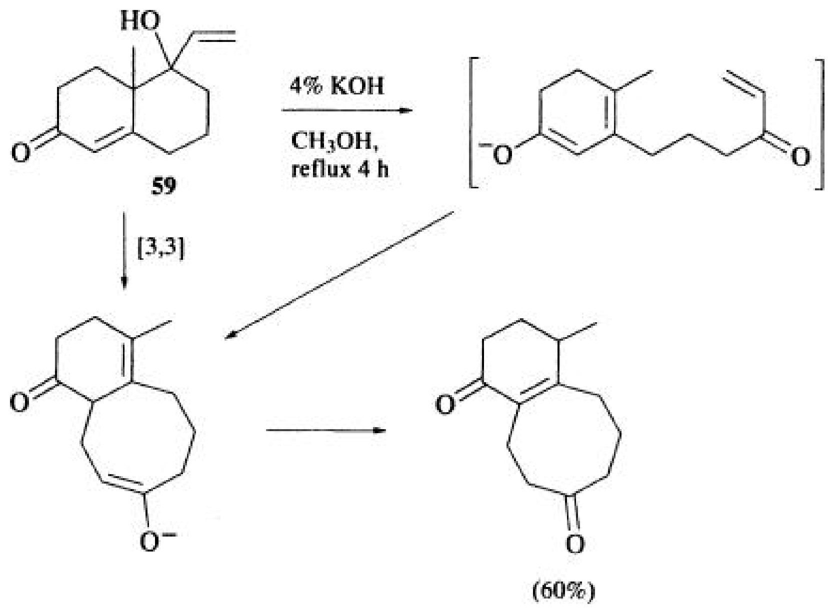
3.1.1.6. 3-Methylene-1-vinylcycloalkanols

The rearrangement of alcohol **59** to produce a ring-expanded product in 60% yield was initially proposed to involve cleavage of the alkoxide followed by Michael addition. However, formation of an eight-membered ring in such a facile process by a concerted, anion-assisted [3,3]-sigmatropic rearrangement seems a more likely possibility. The very mild conditions are understandable since the carbon–carbon bond cleavage required for the rearrangement is accelerated by the anion-stabilizing carbonyl group (Eq. 74). (86-88)

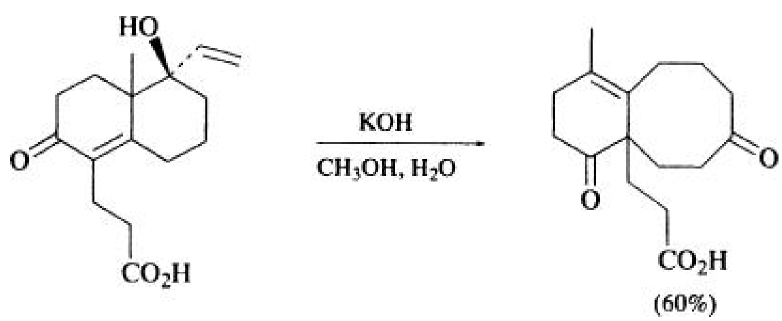
Other examples of this type of reaction include the rearrangement in Eq. 75. Often, the initial [3,3]-sigmatropic rearrangement product undergoes further basecatalyzed cyclization. Thus the transformation of ketone **60** (Eq. 76) to bridged ketone **61** in quantitative yield involves isomerization of the intermediate enolate followed by aldol cyclization.

Equation 77 illustrates the extension of the anion-assisted [3,3]-sigmatropic rearrangement to ethynyl carbinols. (89) This type of Cope rearrangement has also been studied with chiral substrates (Eq. 78). Isomerization of optically active **62** with retention of configuration is observed when the reaction is induced with potassium hydride in tetrahydrofuran. However, the

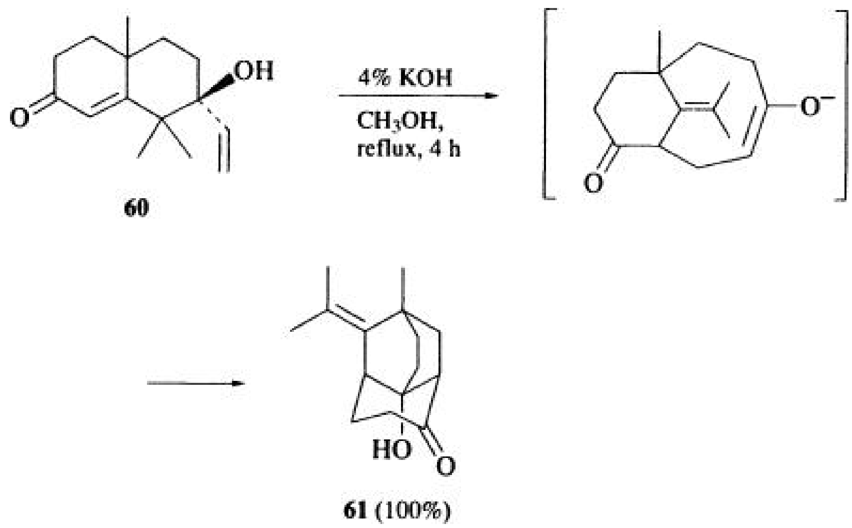
[3,3]-sigmatropic rearrangement leads to racemic product under protic conditions (sodium methoxide in methanol). Thus the



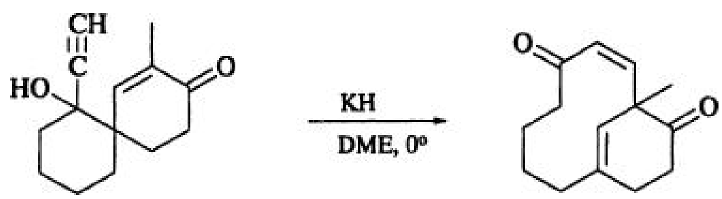
(74)



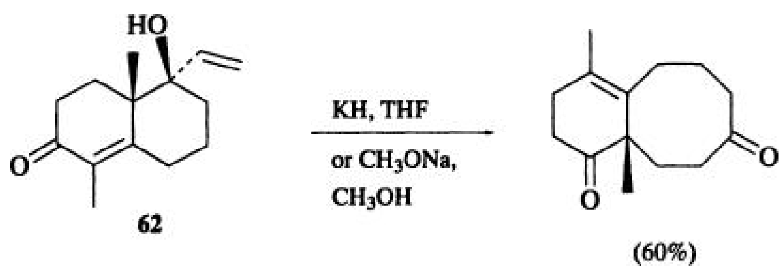
(75)



(76)



(77)

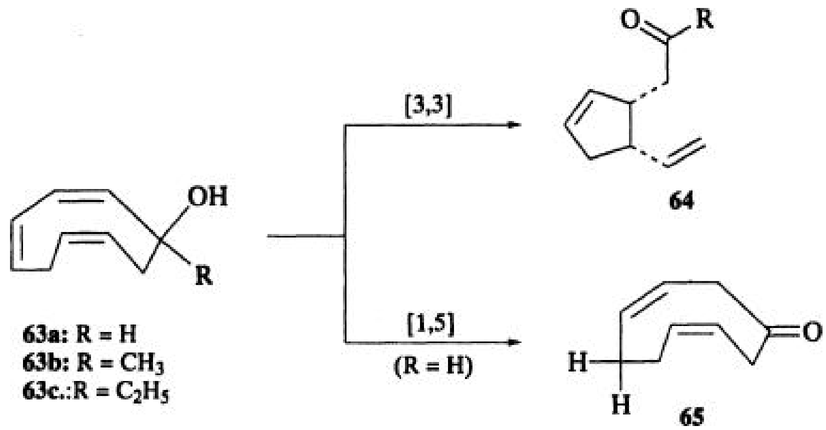


(78)

two alternative mechanisms described in Eq. 74 both appear to operate. (90, 91) Studies in this series have been reviewed. (92)

3.1.1.7. Cope Rearrangements that Contract Medium-Sized Rings

The few examples of [3,3]-sigmatropic rearrangement reactions that lead to overall ring contraction involve nine-membered rings (Eq. 79). (30, 93-94a) Because the substrates are derived from 1,5-cyclooctadiene, a double bond not strictly necessary for the Cope rearrangement is always present. This double bond sometimes causes complications arising from [1,5]-hydrogen migrations and elimination reactions.



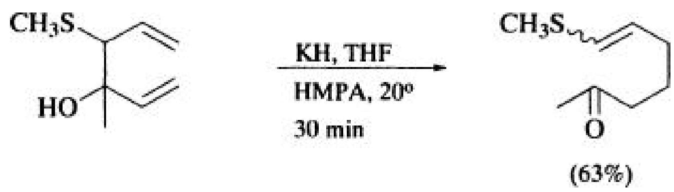
(79)

These eliminations are discussed in more detail in the section on Common Side Reactions. When alcohol **63a** is heated for 3 hours in benzene in a sealed tube, smooth conversion ensues, affording a mixture of 80% ketone **65** and 20% ring-contracted aldehyde **64a** (Eq. 79). This result reflects a kinetically favorable [1,5]-hydrogen shift that predominates over the oxy-Cope process. When alcohols **63a–c** are treated with 1.2 equivalents of potassium hydride in tetrahydrofuran at room temperature, the exclusive products are those of the anion-accel erated oxy-Cope rearrangement. Kinetic studies show that the anticipated acceleration of the two sigmatropic processes by a potassium alkoxide is greater for the [3,3] rearrangement (by factors of 10^{10}–10^{11}) as compared to the [1,5]-hydrogen shift (10^{5}–10^{6}). (94b)

3.1.1.8. Rearrangements of Sulfur-Substituted Substrates

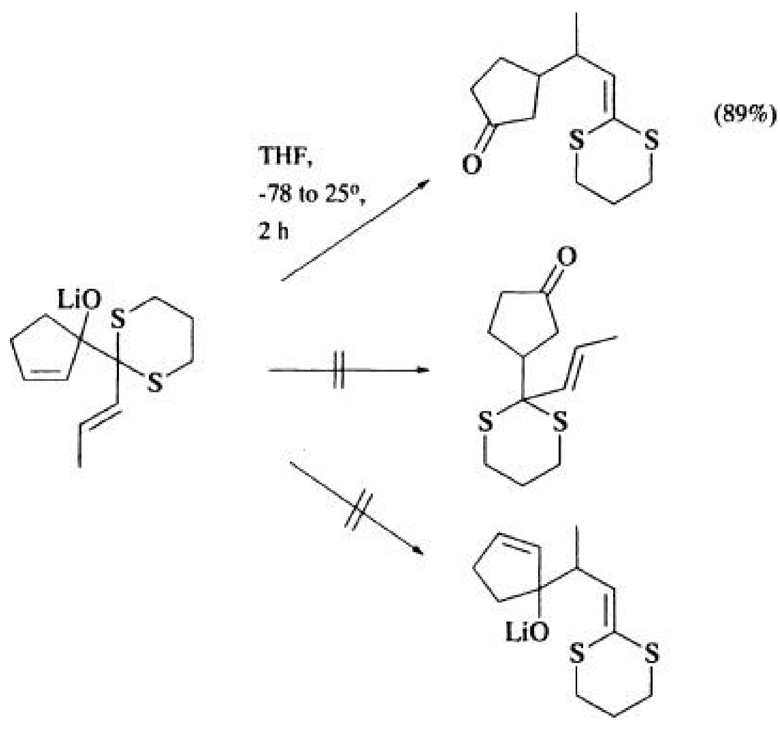
Since the acceleration of sigmatropic rearrangement reactions depends on the polarized bond-breaking step (Eq. 80), it is not surprising that the introduction of a carbanion-stabilizing group such as an alkylthio group facilitates the reaction. The rearrangement of the simplest system (Eq. 81) proceeds at room temperature. 21 Direct comparison of the rates of rearrangement with and without sulfur substitution is discussed earlier (Eq. 61).

(80)



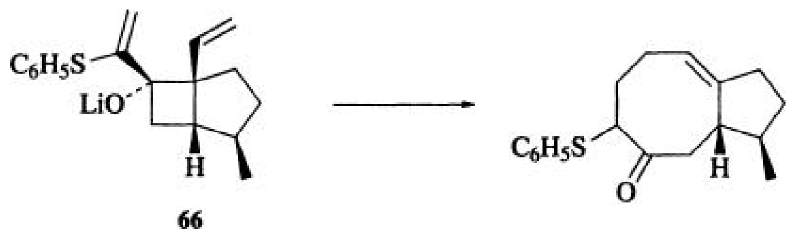
(81)

Although the reaction of Eq. 82 possesses the potential for alternative [1,3]-sigmatropic rearrangements, only the [3,3]-sigmatropic rearrangement is observed. (95)

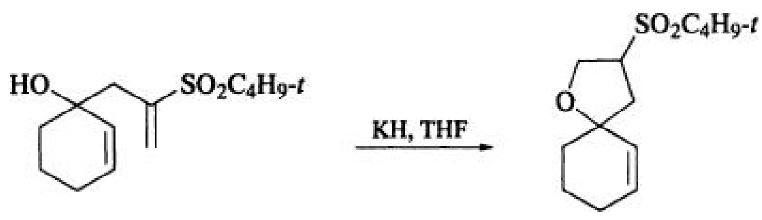


(82)

When the sulfur substituent is not directly on the carbon–carbon bond involved in the rearrangement, such as in alkoxide **66**, the substituent has little effect on the reaction rate (Eq. 83). 70 A related substituted system, however, does not rearrange but instead undergoes Michael addition to produce a cyclic ether (Eq. 84). (96)



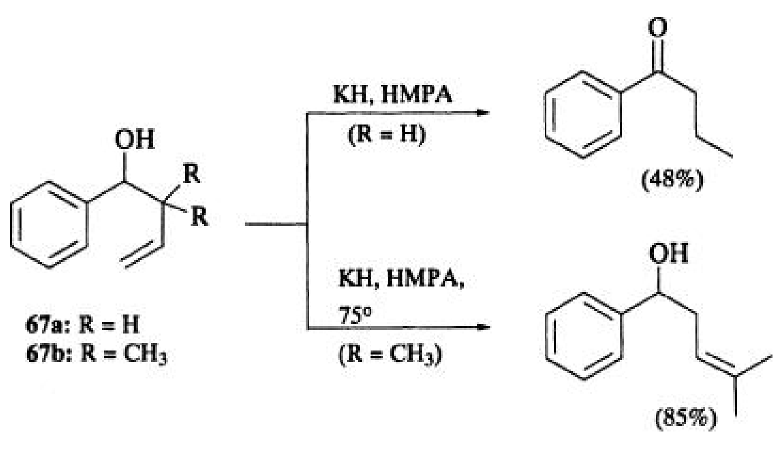
(83)



(84)

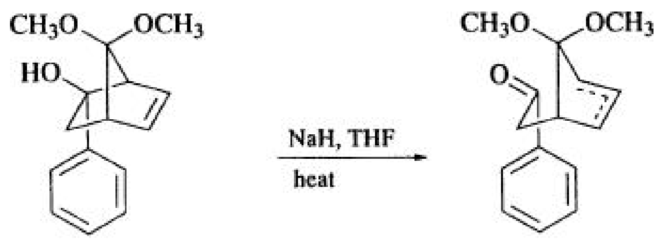
3.1.1.9. Cope Rearrangements that Involve Aromatic Bonds

The “aromatic Cope rearrangement” of 4-phenyl-1-butene has not been observed, presumably because of its high activation energy. Attempts to force participation of the aromatic ring in an anion-assisted [3,3]-sigmatropic process leads to either double bond isomerization (**67a**), or the alternative [1,3]-sigmatropic rearrangement (**67b**, Eq. 85). (97) Incorporation



(85)

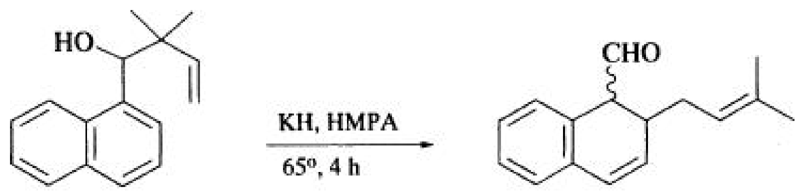
of the 4-phenyl-1-butene system into a strained ring results in cleavage (Eq. 86). (54)



(10%)

(86)

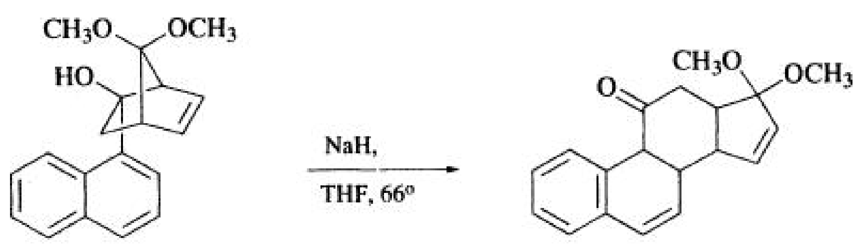
The participation of aromatic double bonds does occur in less highly resonance-stabilized systems. The naphthylcarbinol **68** isomerizes to produce the rearranged aldehyde in low yield (Eq. 87). (97) When the bond that cleaves is contained within a strained ring, the isomerization is faster and proceeds in higher yield; the less highly ionized sodium salt can be used in this reaction (Eq. 88). (54)



68

(10%)

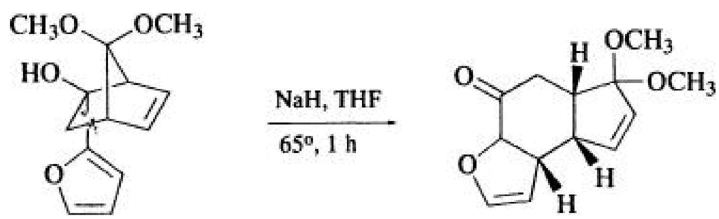
(87)



(75%)

(88)

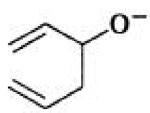
Participation of the furan ring is observed in the strained bicyclo[2.2.1] system (Eq. 89). 54,56 No examples of rearrangements involving simple furans are known. Unsuccessful participation of a furan in a 1,3-sigmatropic shift is described in Eq. 169.



(89)

3.1.1.10. Solvent-Induced [3,3]-Sigmatropic Rearrangements

The formation of a fully charged alkoxide such as **69** is certain to greatly accelerate a reaction like the Cope rearrangement. Partial ionization of the alcohol proton by hydrogen bonding to a basic solvent as in complex **70** should also accelerate the Cope rearrangement although less strongly.



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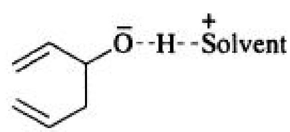
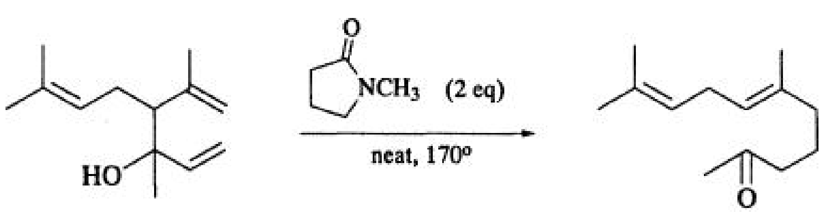


70

When alcohol **71** is heated in the presence of varying amounts of the polar solvent *N*-methyl-2-pyrrolidone, a small increase in the rate of the [3,3]-sigmatropic shift and a great decrease in the fragmentation side reaction (Eq. 90) are observed. (98)

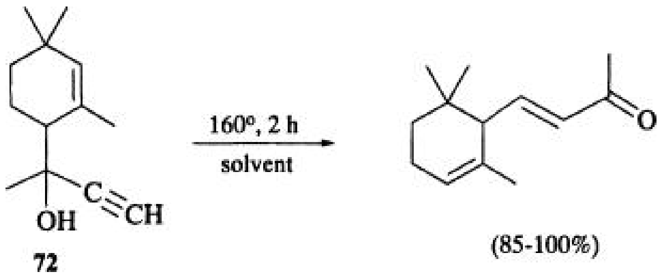


71

(—)

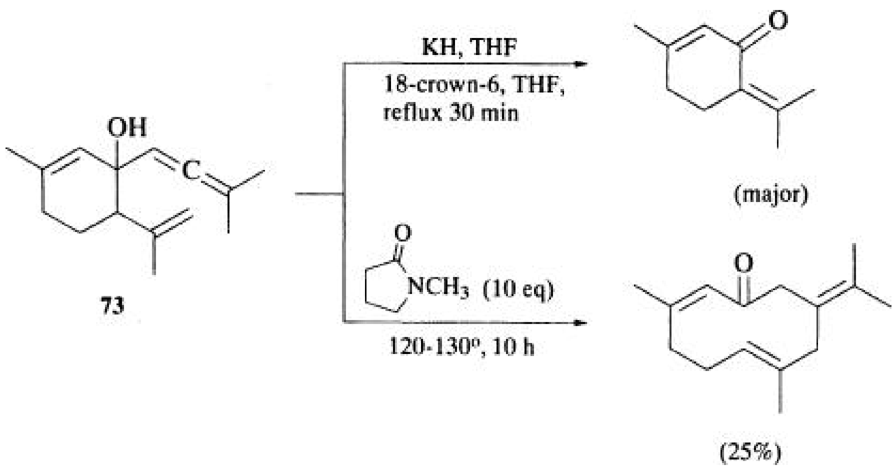
(90)

A similar effect is seen in the [3,3]-sigmatropic rearrangement of alcohol **72** (Eq. 91), which under otherwise identical conditions rearranges in *n*-decane, *N*-methylpyrrolidinone, and hexamethylphosphoric triamide in 85%, 90%, and 100% yields, respectively. (99)



(91)

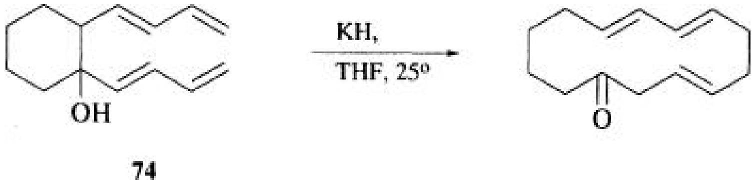
Alcohol **73** only undergoes fragmentation when treated with base (Eq. 92). (100) No reaction occurs on pyrolysis of its trimethylsilyl ether at 150°. On the other hand, heating alcohol **73** in 1-methyl-2-pyrrolidinone at 120–130° leads to the oxy-Cope rearrangement in 25% yield. No applications of such solvent effects to the other classes of sigmatropic rearrangements have been reported. It is likely that such effects will also be seen in other symmetry-allowed processes.



(92)

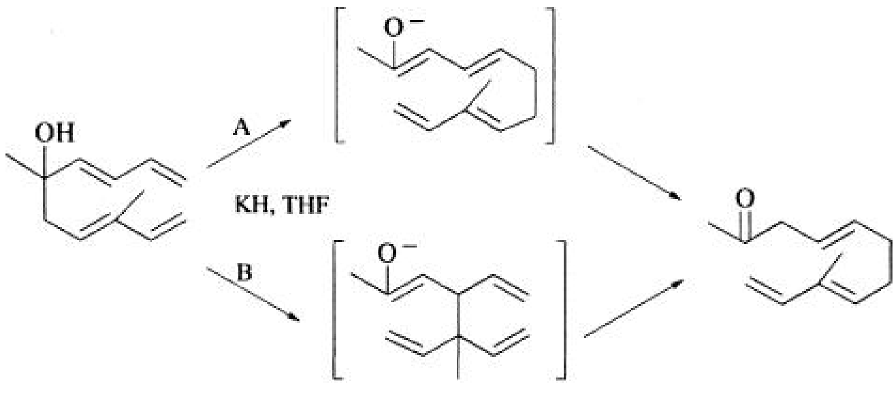
3.2. [5,5]-Sigmatropic Rearrangements

Rearrangement of the potassium salt of alcohol **74** proceeds at room temperature to yield a 14-membered cyclic trienone in 90% yield (Eq. 93). (101) This process involves



(93)

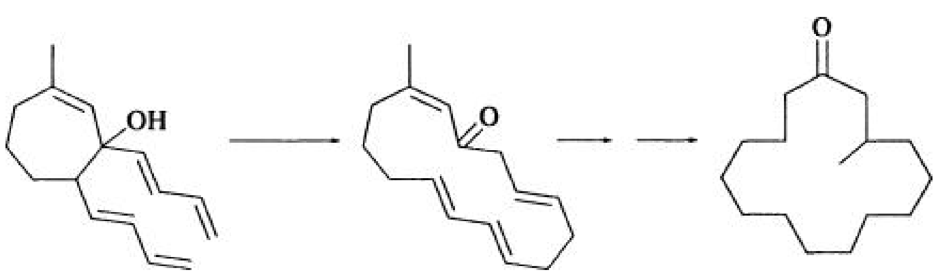
an oxyanion-assisted [5,5]-sigmatropic rearrangement which results in an eight-carbon ring expansion (Eq. 94, pathway A). The reaction conditions are the same as (or slightly milder than) those in the analogous [3,3]-sigmatropic rearrangement (e.g., Eq. 28). An alternative pathway involving two sequential anion-accelerated [3,3]-sigmatropic rearrangements (pathway B) was initially considered unlikely on the basis of kinetic arguments: the overall rate of the reaction in Eq. 94 ($t_{1/2}$ = 1.8 minutes at 25°) was thought to be much too high to proceed via enolate **75**. (102) The second stage of pathway B in Eq. 94 would involve a carbanion-accelerated



(94)

[3,3]-sigmatropic rearrangement. Pathway B is implicated in generating part of the products. (82) A few other examples of rearrangements involving assistance by carbanions are discussed in the section on Miscellaneous Reactions.

An anion-assisted [5,5]-sigmatropic rearrangement is the key step in a synthesis of the 15-membered cyclic ketone muscone (Eq. 95). (40)



(95)

3.3. [1,3]-Sigmatropic Rearrangements

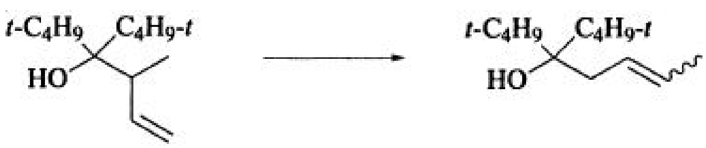
3.3.1.1. Allylcarbinols

The [1,3]-sigmatropic rearrangement of homoallylic alcohols (Eq. 96) is a major class of concerted reactions allowed by the Woodward–Hoffmann

(96)

rules. Substrate and product in Eq. 96 correspond to the two possible regioisomers resulting from addition of an allylic anion to a carbonyl group. Because of the widespread use of the Grignard reaction, this rearrangement has been well studied.

Addition of crotylmagnesium bromide in tetrahydrofuran to hindered ketones such as di-*tert*-butyl ketone generally leads only to isomer **77** (Eq. 97). Alcohol **76**



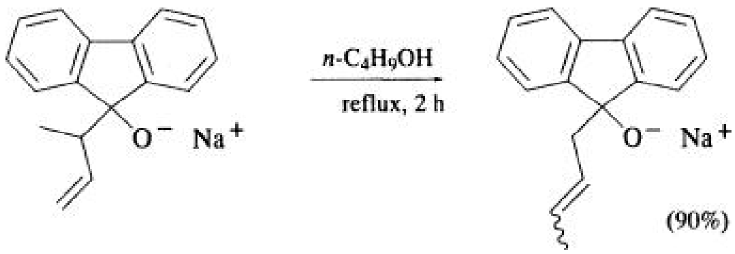
(97)

76 **77**

can be prepared by another route; it rearranges to isomer **77** as the magnesium bromide salt at –78° in tetrahydrofuran or at higher temperatures in diethyl ether. (18) Solvent polarity, counterion effects, and steric hindrance all contribute to rate acceleration in the manner discussed for [3,3]-sigmatropic rearrangements. Another example is shown in Eq. 98. (97) An alternative “reverse Grignard” mechanism involving fragmentation to the carbonyl compound and the allylic anion has been proposed. (103) This mechanism, however, does not account for the success of the rearrangement

(98)

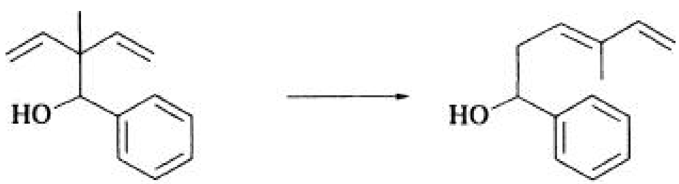
in macrocyclic ring expansions (Table XVI) or the isomerization in protic solvents (Eq. 99). (104) Anion-assisted [1,3]-sigmatropic rearrangements are, however, more prone to fragmentation side reactions than the corresponding Cope rearrangements. (103)



(99)

3.3.1.2. 3-Alkoxyalkyl-1,4-dienes

The rearrangements of the carbonyl adducts to 1,3-pentadienyl anions form a related class of [1,3]-sigmatropic rearrangements. Alcohol **78** isomerizes smoothly as the lithium salt in tetrahydrofuran at reflux or within 5 minutes at 0° as the potassium salt (Eq. 100). (105) The additional double bond facilitates

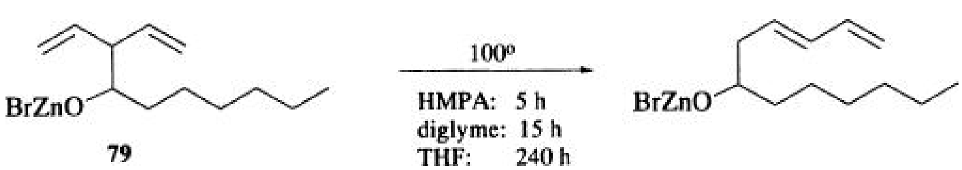


(100)

78

polarized bond breaking. Thus the isomerization of the analogous system where one of the vinyl groups is replaced by a methyl group (Eq. 98) requires prolonged heating of the potassium salt in hexamethylphosphoric triamide.

The effect of solvent polarity on the isomerization is illustrated for salt **79** (Eq. 101). (106) When an alternative [3,3]-sigmatropic rearrangement pathway is possible, this mode of reaction is preferred (Eqs. 102, 103). (105, 106)



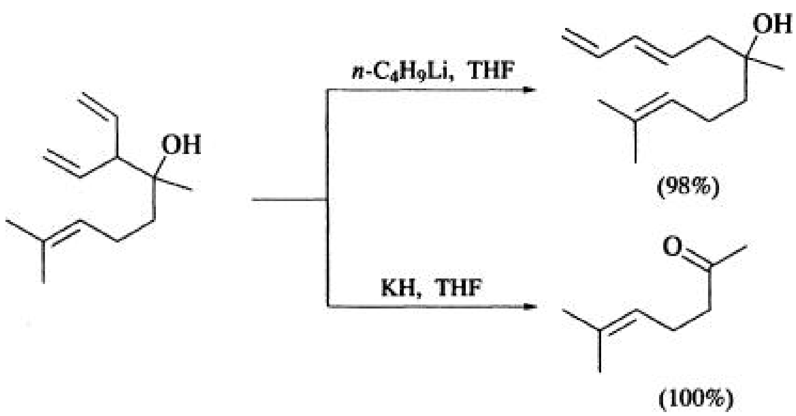
79

(101)

(102)

(103)

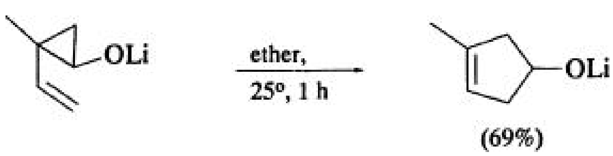
The competing fragmentation pathway, which predominates when the potassium salt is employed, can be suppressed by use of the less ionic lithium salt (Eq. 104). (107)



(104)

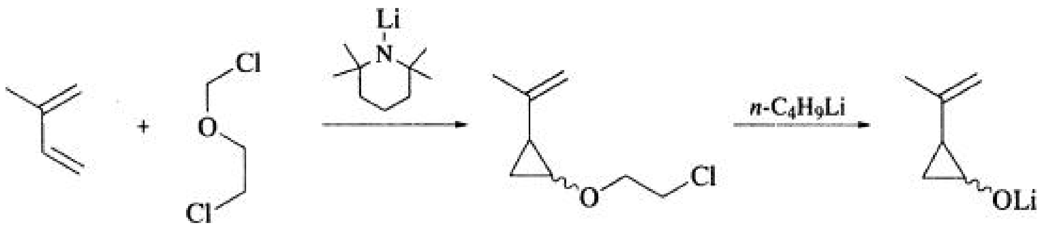
3.3.1.3. 2-Vinylcyclopropanols

One of the best known examples of a thermal [1,3]-sigmatropic rearrangement is the vinylcyclopropane rearrangement. (108) High temperatures (frequently 500–600°) are required for this reaction. Placement of an alkoxy substituent on the cyclopropane ring allows the reactions to proceed at room temperature (Eq. 105). (109)



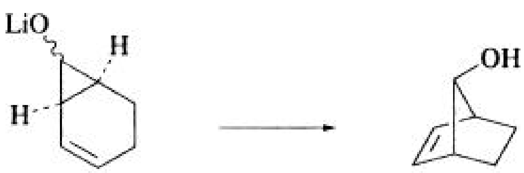
(105)

A synthesis of cyclopropanols has been developed specifically to exploit this reaction. Addition of carbenoids to dienes leads to β -chloroethyl ethers of the required cyclopropanols (Eq. 106). These are cleaved by reaction with excess *n*-butyllithium (5 equivalents) in diethyl ether at room temperature to produce the corresponding lithium alkoxides. (110) In some reactions, these salts isomerize spontaneously to the corresponding cyclopentanols (Eq. 105). Otherwise, hexamethylphosphoric triamide is added, and the isomerization is complete within 1–2 hours at 25–50°.



(106)

Except for substrates with substituents *cis* to the vinyl group, the reactions proceed with high selectivity. For example, [1,3]-sigmatropic rearrangement of salt **80** leads exclusively to *anti*-bicyclo[2.2.1]hept-2-en-7-ol (Eq. 107). (26)

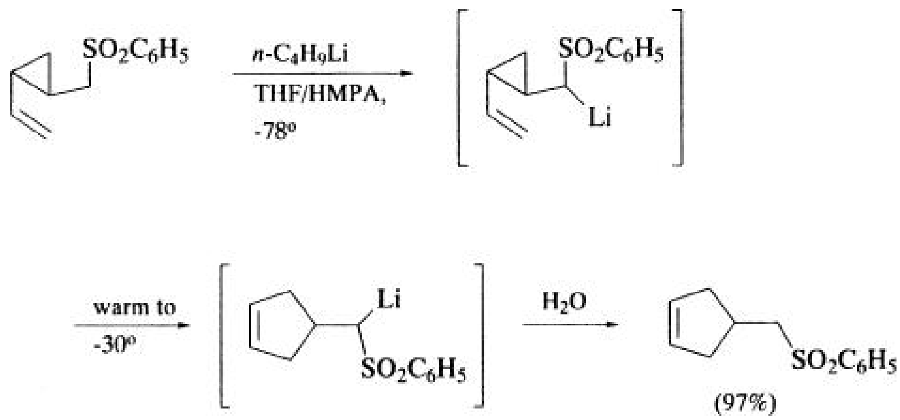


80

(45%)

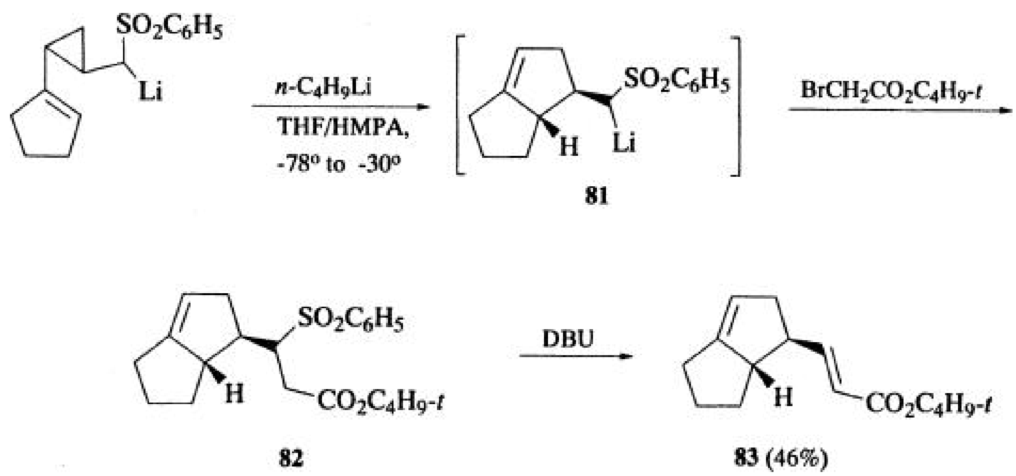
(107)

The scope of the anion-assisted vinylcyclopropane rearrangement, however, is limited by the availability of cyclopropanols. An alternative route involving direct oxidation of lithiocyclopropanes has been used, (111) but its potential has not been extensively explored. An interesting extension of the process uses a carbanion adjacent to the bond that shifts to promote the [1,3]-sigmatropic process (Eq. 108). (83) This



(108)

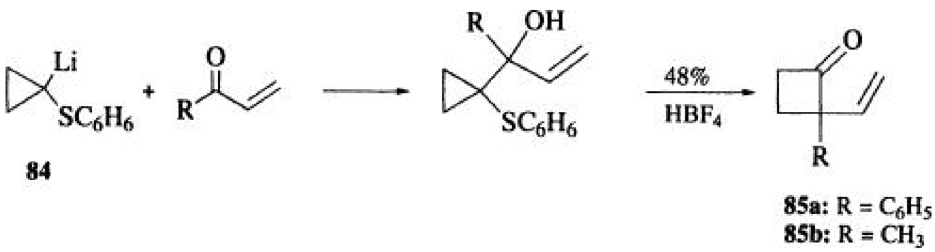
rearrangement is faster than the analogous oxyanion-induced process, but is less stereochemically selective. It is synthetically useful because the anionic product can be trapped with electrophiles. For example, the rearranged carbanion **81** is trapped by alkylation with *tert*-butyl bromoacetate. Treatment of sulfone **82** with diazabicycloundecene (DBU) induces elimination to conjugated ester **83** (Eq. 109). (83)



(109)

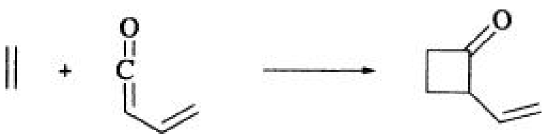
3.3.1.4. 2-Vinylcyclobutanols

In contrast to the dearth of methods for the synthesis of cyclopropanols, there are two well-developed routes to the 2-vinylcyclobutanols required for anion-assisted rearrangement. One involves addition of lithiocyclopropanes such as **84** to enones followed by acid-induced ring expansion (Eq. 110). (68)



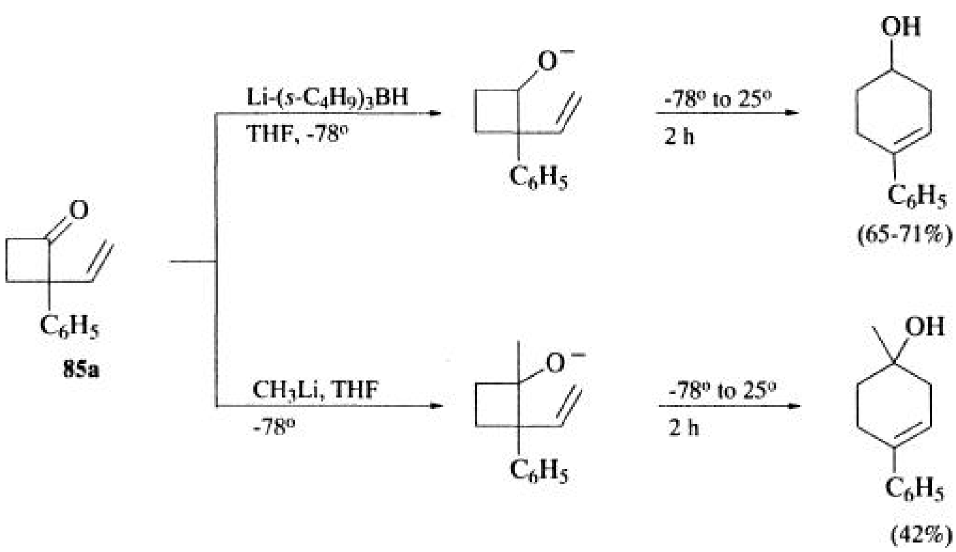
(110)

The second is based on [2 + 2] cycloadditions of olefins to vinylketenes (Eq. 111). (112) In addition, cyclobutanones and cyclobutanols are much more stable



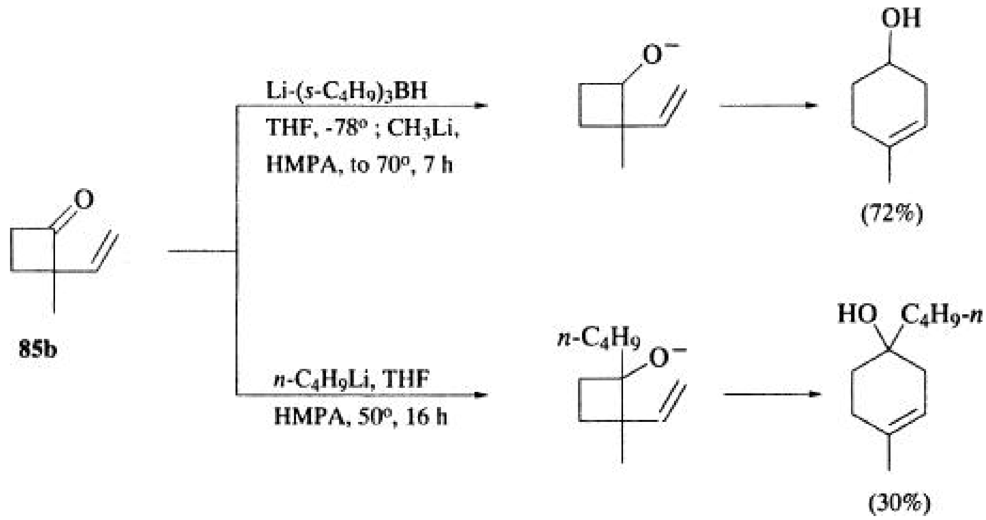
(111)

than their three-membered analogs. Reduction of aryl ketone **85a** with 2 equivalents of lithium tri(*sec*-butyl)borohydride in tetrahydrofuran at –78° gives an anion which rearranges to the corresponding cyclohexanol on warming to room temperature (Eq. 112). The anion obtained by addition of methyllithium to ketone **85a** also isomerizes at room temperature (Eq. 112). (112)



(112)

By contrast, the anion derived by reduction of methyl ketone **85b** (Eq. 113) does not rearrange under these conditions, but requires conversion of the borate complex



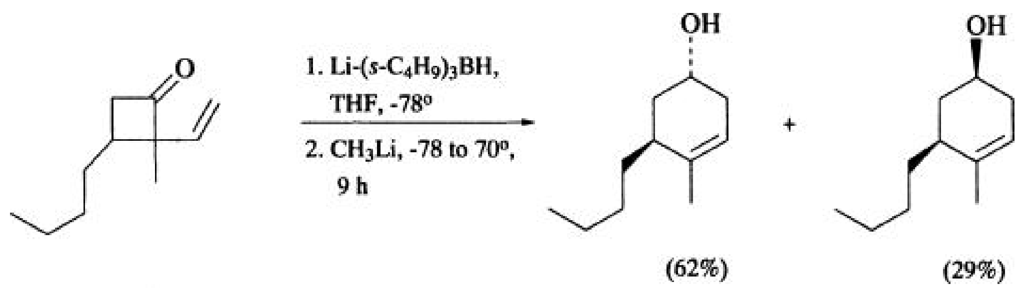
(113)

with excess methyllithium to the free lithium salt, followed by addition of hexamethylphosphoric triamide and heating to 70° for 7 hours. The lithium salt produced by addition of *n*-butyllithium to ketone **85b** (Eq. 113) is also stable in tetrahydrofuran at room temperature and requires warming with hexamethylphosphoric triamide in order to undergo the [1,3]-sigmatropic rearrangement. (112) The effect of the counterion and solvent on the rate and the beneficial influence of an additional anion-stabilizing group (the phenyl group) in ketone **85a** are typical of the isomerization processes described in this chapter.

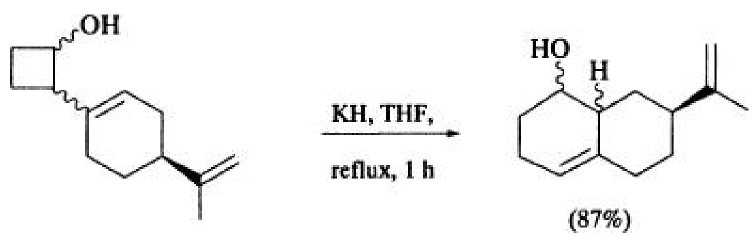
In the more congested system shown in Eq. 114, rearrangement of the lithium salt in tetrahydrofuran and hexamethylphosphoric triamide requires heating to 70° for 90 hours; the potassium salt rearranges rapidly at room temperature under these conditions. (112)

(114)

Complex substrates often give mixtures of isomers (Eq. 115), (112) (Eq. 116), (113) although the good overall yield and unique nature of this synthetic transformation make the method a valuable one.

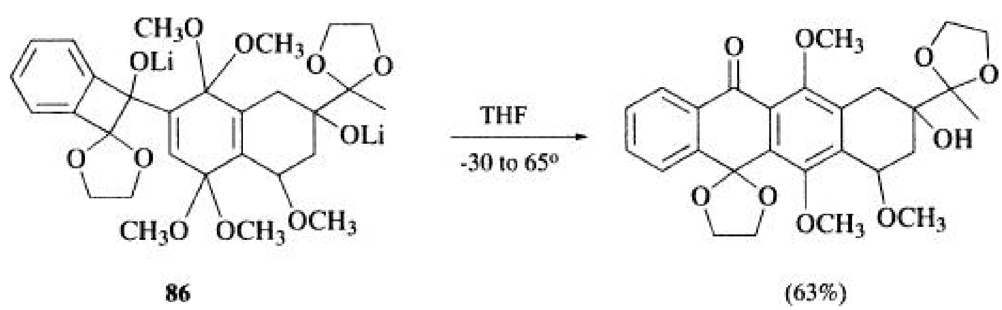


(115)



(116)

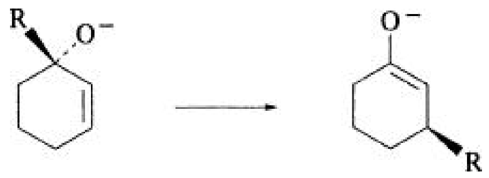
A [1,3] shift has been applied in the synthesis of anthracyclinones (Eq. 117). (114) The lithium salt **86**, formed in situ from a cyclohexenyllithium precursor, undergoes [1,3]-sigmatropic rearrangement and subsequent aromatization in 63% yield. Rearrangement under relatively mild conditions (lithium salt in tetrahydrofuran) is probably due to relief of strain in the cyclobutane ring.



(117)

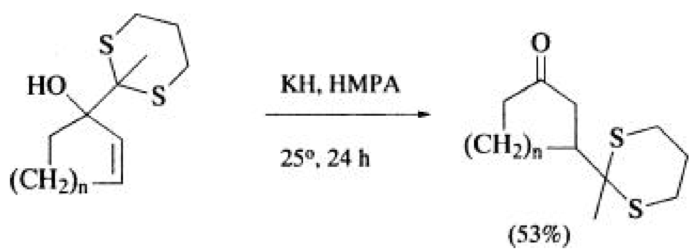
3.3.1.5. 1-Substituted 2-Alkenols

Equation 118 shows the conversion, by [1,3]-sigmatropic rearrangement, of the 1,2 adduct of an anion to an α , β -unsaturated



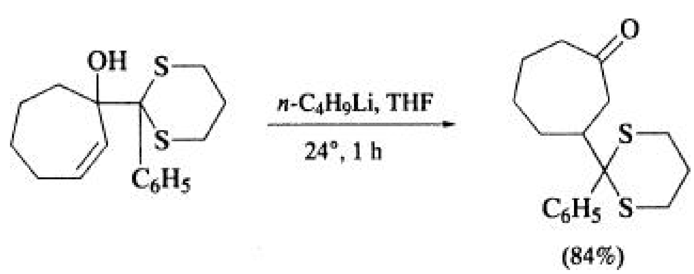
(118)

ketone into the 1,4 adduct. Examples of this useful rearrangement are known for five-, six-, and seven-membered rings. 21,115–120 For the reaction to succeed, sufficient anion-stabilizing groups must be present on the C - C bond that is cleaved. The isomerizations in Eq. 119 require the formation of the potassium salts in hexamethyl-phosphoric triamide,



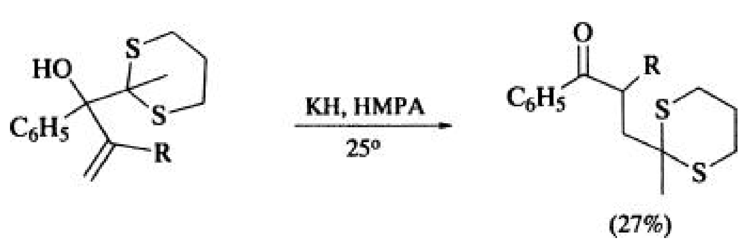
(119)

whereas a related substrate that has the additional anion-stabilizing phenyl ring undergoes the [1,3] shift as the lithium salt (Eq. 120). (115, 119) A



(120)

few examples of acyclic systems are known (Eqs. 121, 122), but the yields are uniformly low. (115, 120, 121) Fragmentation is a common and serious side reaction in this particular variant of a [1,3]-sigmatropic shift.



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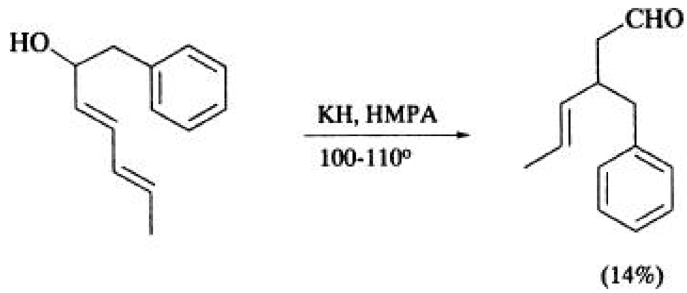
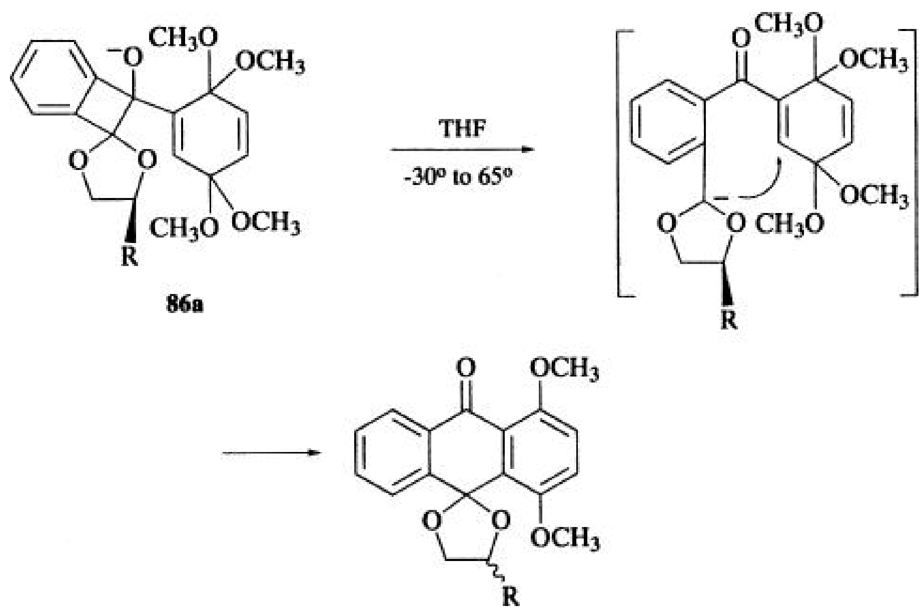


(122)

The loss of stereochemistry observed in the [1,3] shift of the chiral ketal **86a** provides evidence for a nonconcerted rearrangement (Eq. 123). (50) A mechanism involving an intermediate anion is suggested.

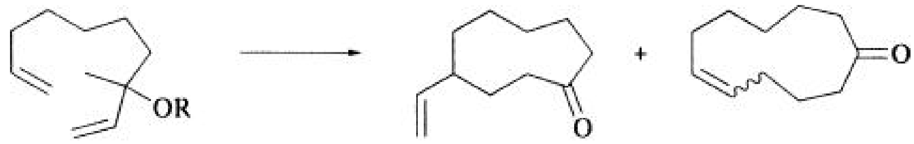


(123)

There are probably many more classes of substrates that will undergo this type of [1,3] isomerization. Examples are known where the migrating group is tin (117) or a protected cyanohydrin derivative. (118)

3.3.1.6. Macrocyclic Systems

The thermal oxy-Cope rearrangement of certain 1,5-dienes is an unfavorable process. Pyrolysis of the trimethylsilyl ether of alcohol **87** (R = H) at 280° gives the product **88** of a [3,3] shift in only 11% yield (Eq. 124). (122)



(124)

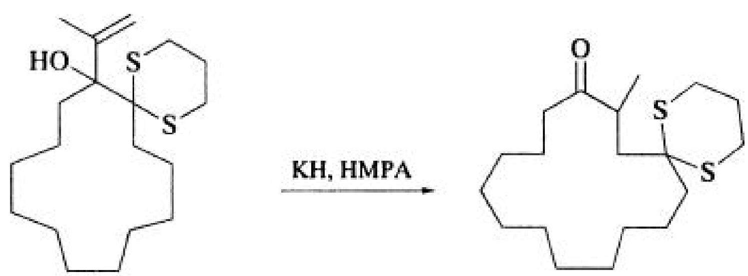
87		**88**	**89**
R			
$Si(CH_3)_3$	280° ($t_{1/2}$ = 2.3 h)	(11%)	(80%)
K	HMPA, 25°, 3 h	(6%)	(49%)

The major products, isolated in 80% yield, are the [1,3] shift products **89** (*cis*:*trans* = 83:17). Treatment of alcohol **87** (R = H) with potassium hydride in hexamethylphosphoric triamide leads to rearrangement at room temperature. The reaction is complete in 3 hours, and the ratio of products **88** and **89** is similar to that of the thermal reaction except that the *cis/trans* ratio in ketone **89** is 60:40. (122, 123) This result is typical of a number of medium and large ring substrates, where for conformational reasons the [3,3]-sigmatropic shift is less favorable than the [1,3] shift.

If the bond that shifts is benzylic (Eq. 125) (124) or substituted with functionalities known to stabilize carbanions (Eq. 126), [1,3] isomerization also occurs, but the yields are modest (20–94%). (See Table XVI for more examples.)

(125)

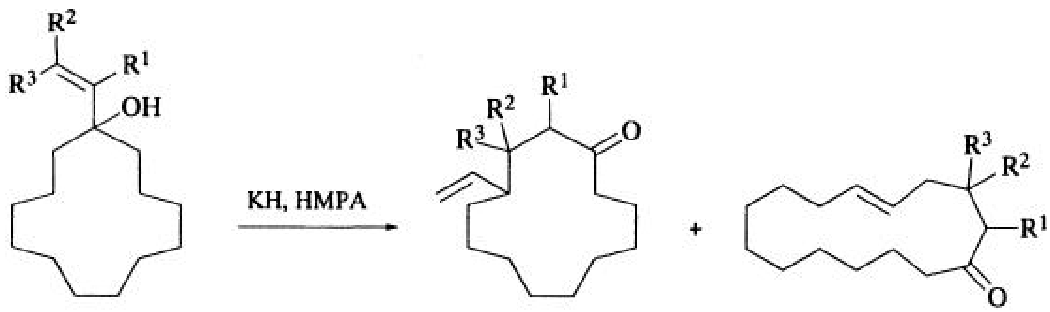
(38%)



(126)

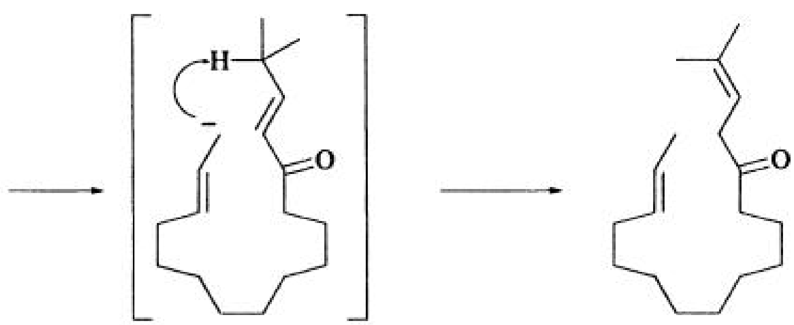
(28%)

The effect of substituents on the relative rates of [1,3] shifts vs. [3,3] shifts in alcohols **90** is shown in Eq. 127. (125) Significant effects are seen only for substituents on the terminus of the vinyl group. In addition, a major side reaction in the isopropyl derivative **90e** is fragmentation to give ketone **93**, presumably derived by proton transfer in an intermediate allyl anion (Eq. 128). (125)



91 92 (127)

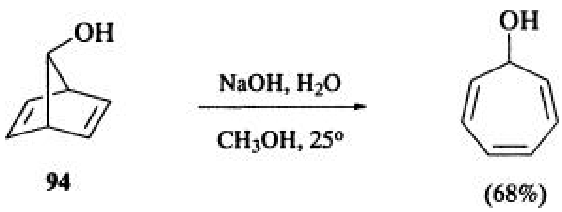
	R^1	R^2	R^3	91 : 92	
90a:	H	H	H	87 : 13	(70%)
90b:	CH_3	H	H	82 : 18	(62%)
90c:	H	CH_3	H	45 : 55	(39%)
90d:	H	H	CH_3	54 : 45	(62%)
90e:	H	$i\text{-}C_3H_7$	H	27 : 35	(69%)

90e  (128)

93

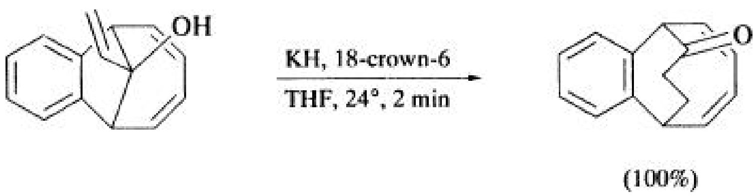
3.3.1.7. Bridged Bicyclic Carbinols

The [1,3]-sigmatropic rearrangement is especially facile and high yielding in rigid systems, which presumably are most favorable for orbital overlap. An early example was discovered during an attempted base-catalyzed alkylation of the alcohol **94** (Eq. 129). (126) The anion-assisted reaction is 10^4 times

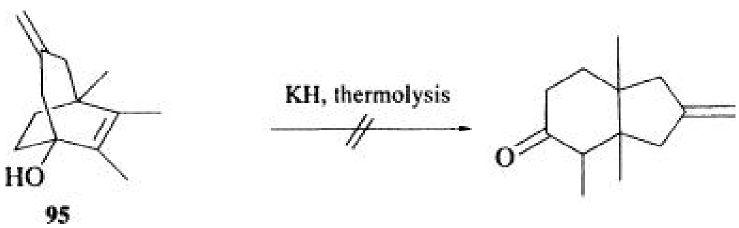


(129)

faster than the thermal process. The corresponding ether requires heating to 170°. A detailed study of another example (Eq. 130) has been reported. (127) The attempted isomerization of alcohol **95** gives no detectable product of a [1,3] shift (Eq. 131),

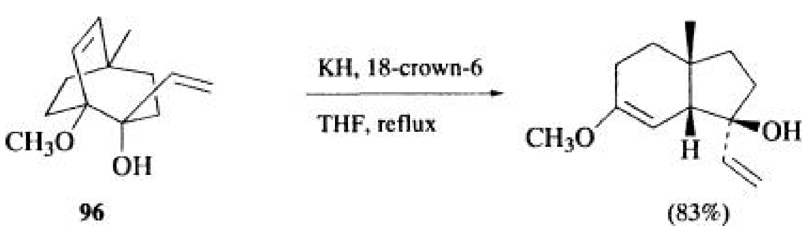


(130)

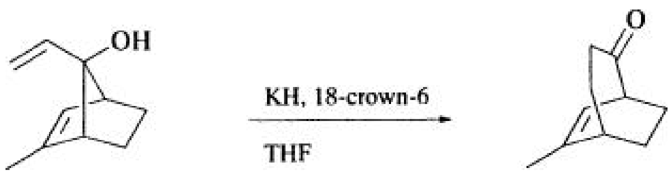


(131)

probably because of very poor overlap of the migrating σ bond with the allylic framework. (128) Bicyclic carbinol **96** does not undergo the possible [3,3]-sigmatropic rearrangement, but instead gives the [1,3] shift product with predominant inversion of configuration at the migrating center, as predicted by orbital symmetry (Eq. 132). (129) A number of 7-substituted bicyclo[2.2.1]hept-2-en-7-ols also react predominantly by [1,3] shifts (Eq. 133). (28)



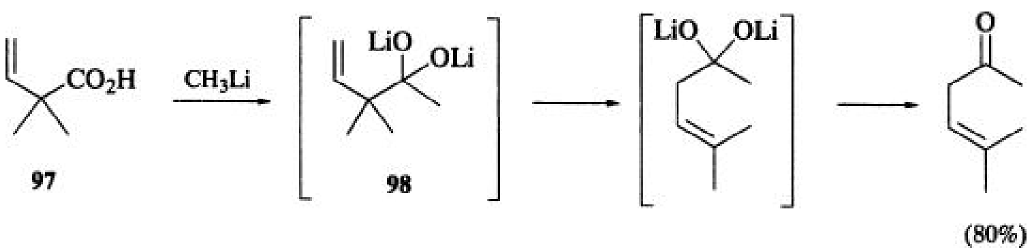
(132)



(133)

3.3.1.8. 1,1-Dialkoxy-Substituted Compounds

All of the anion-assisted reactions discussed so far have only one alkoxide substituent on the bond that breaks. When methyllithium is added to carboxylic acid **97**, a 1,1-dialkoxy intermediate **98** is formed (Eq. 134). (130) These species are known to be stable toward expulsion of lithium oxide to give ketones. In the homoallylic system **98**, [1,3]-sigmatropic rearrangement occurs at a rate that appears to be higher than would be expected if only

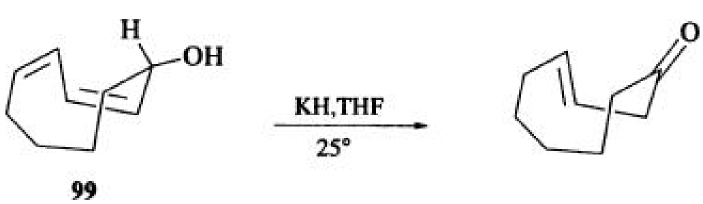


(134)

one alkoxylithium substituent were present, but only two examples of this variant are known. (130, 131)

3.3.1.9. [1,5]-Sigmatropic Shifts

The effect of an alkoxide substituent on an adjacent C - H bond has been calculated to result in substantial bond weakening. (11) The potassium salt of alcohol **99** undergoes a [1,5]-hydrogen shift at ambient temperature (Eq. 135). (30) The anionassisted

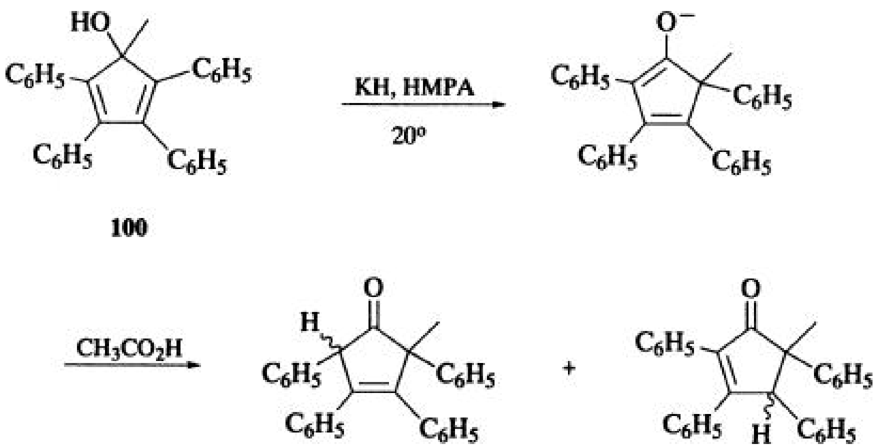


(135)

[1,5]-hydrogen shift is accelerated by a factor of 10^6 over the corresponding purely thermal rearrangement, which requires heating to 160° for 3 hours. Other examples suggest that the hydrogen shift reaction is indeed general. (30, 121) Base-induced side reactions, usually involving transannular deprotonations and double-bond isomerizations, are also observed and are

discussed in the section on Side Reactions.

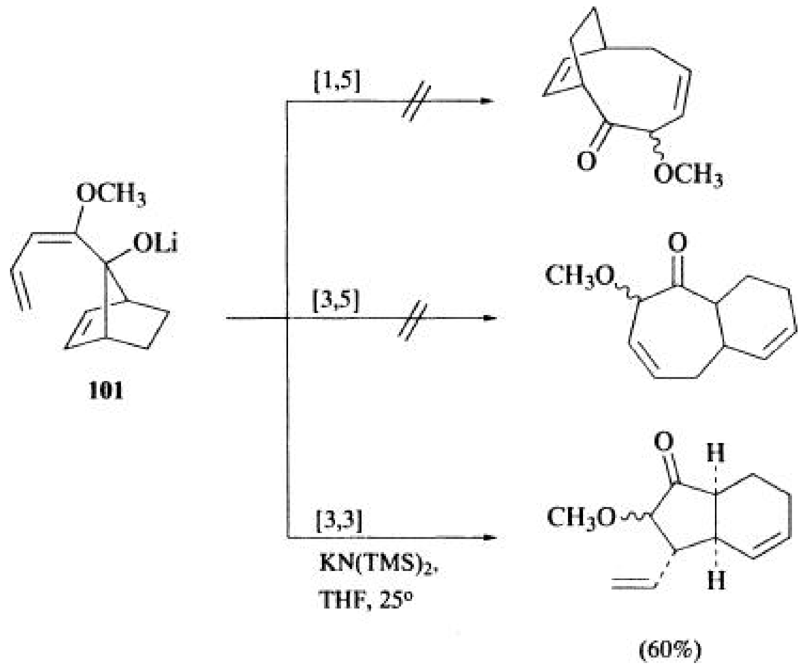
The anion-assisted [1,5]-sigmatropic shift of a methyl group is illustrated in Eq. 136. (132) Other examples involving migration of alkyl, vinyl, and cyclopropyl groups are listed in Table XIX. The thermal uncatalyzed rearrangement of alcohol **100** requires heating to 170°.



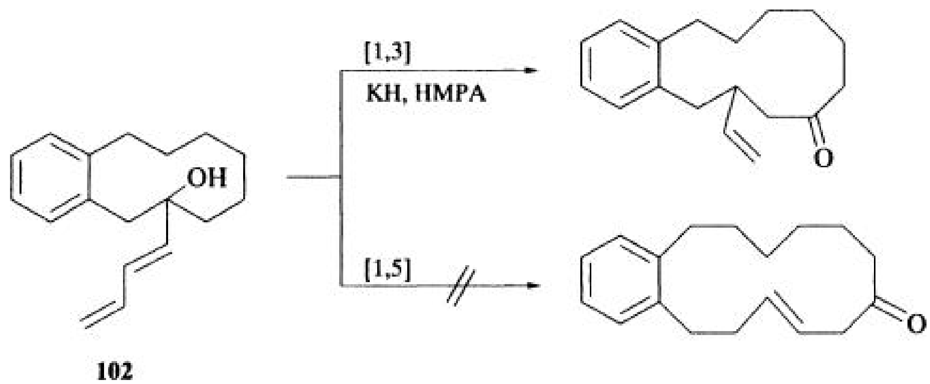
100

(136)

Because of the reluctance of the parent 7-vinylbicycloheptene **24** (*n* = 1,2; Eq. 39) to undergo a [3,3]-sigmatropic shift, the isomerization of compound **101** has been investigated to explore a possible [1,5]- or [3,5]-carbon shift pathway. Only the [3,3]-sigmatropic shift is observed (Eq. 137). (133) Similarly, alcohol **102** rearranges only via a [1,3]-sigmatropic shift (Eq. 138). (123)



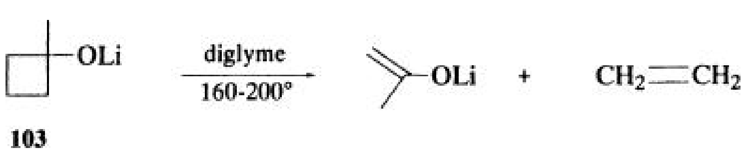
(137)



(138)

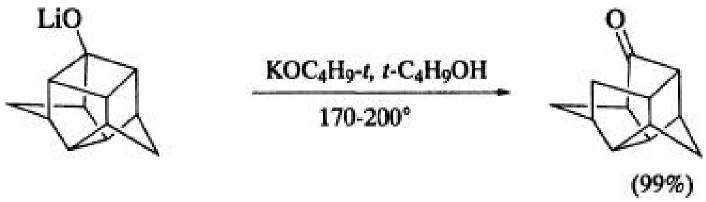
3.4. [2 + 2] Cycloreversions

The fragmentation of a four-membered ring to give two olefins is a symmetry-forbidden process. When lithium salt **103** is heated to 160–200°, cycloreversion occurs to produce an enolate and ethylene (Eq. 139). (29) This reaction is probably quite general although only a few examples are known. (29, 134)



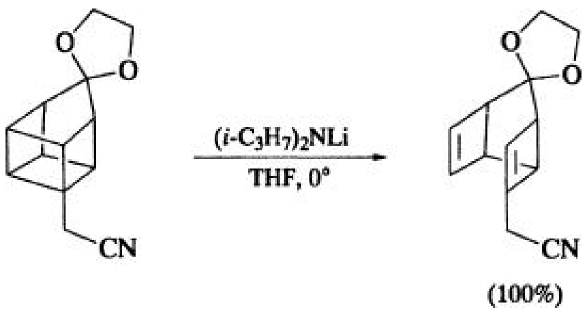
(139)

An alternate path involves the cleavage of only one bond (Eq. 140). (135)

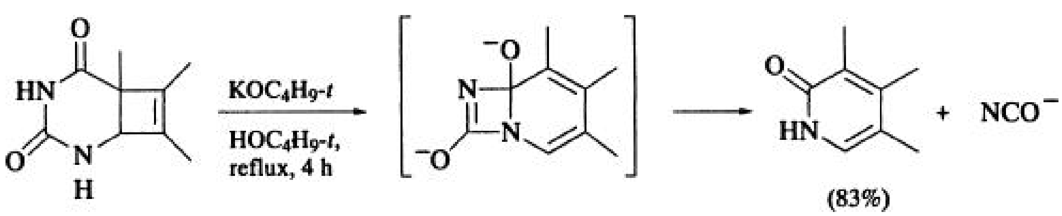


(140)

It is also possible to induce the [2 + 2] cycloreversion with a carbanion (Eq. 141). (136) An example of an anion-assisted [2 + 2] cycloreversion involving expulsion of cyanate is shown in Eq. 142. (137)



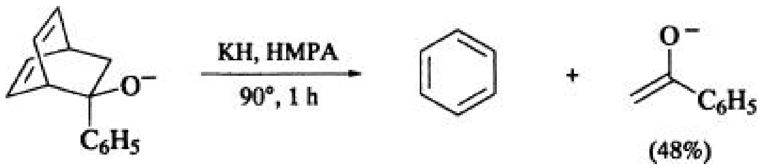
(141)



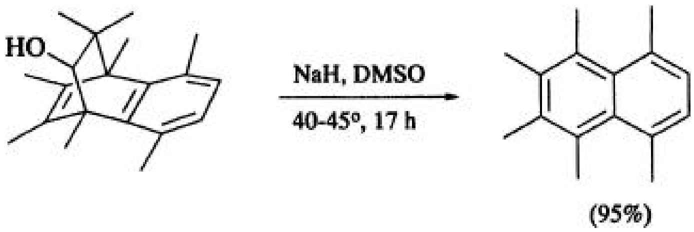
(142)

3.5. [2 + 4] Cycloreversions

The reverse Diels–Alder reaction is of considerable synthetic and mechanistic interest. The thermal reaction usually requires high temperatures. Placement of an oxyanion substituent on one of the bonds that is cleaved generally permits the reaction to be carried out at temperatures below 100° (Eqs. 143, 144). (138, 139)

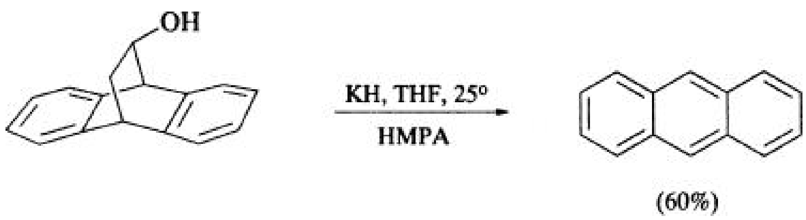


(143)



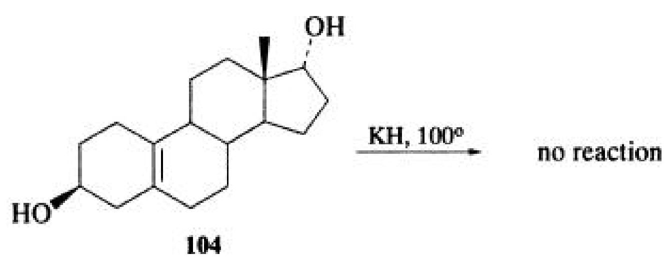
(144)

Careful studies of related systems that produce anthracene derivatives have refined the characteristics required for successful reaction (Eq. 145). (140) The diene

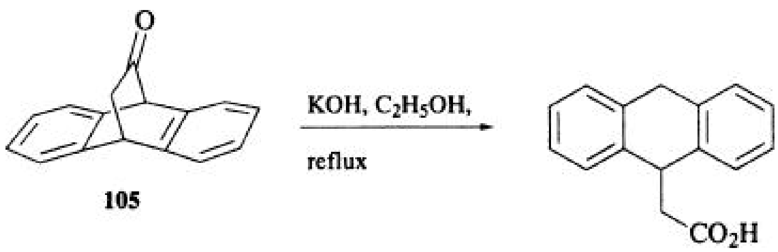


(145)

partner is most commonly an aromatic system, which contributes to the driving force for the reaction. The potassium salt of alcohol **104** is an example where the anion-assisted reverse Diels–Alder reaction fails (Eq. 146). (140) Ketone **105** (Eq. 147) and carbanion **106** (Eq. 148) undergo fragmentation rather than [4 + 2] cycloreversion. (140)

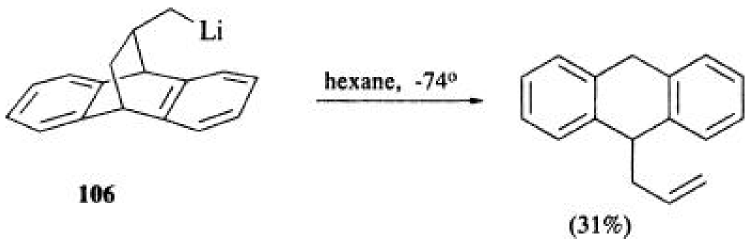


(146)



105

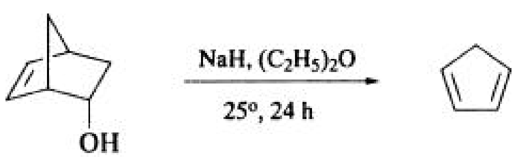
(147)



106

(148)

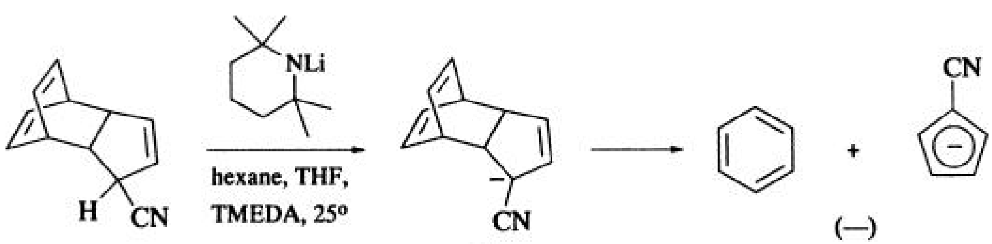
The reverse Diels–Alder reaction of the sodium salt of *endo*-bicyclo[2.2.1]hept-5-en-2-ol (**107**) proceeds smoothly in ether at room temperature (Eq. 149). The *exo* isomer does not react under the same conditions. (141)



107

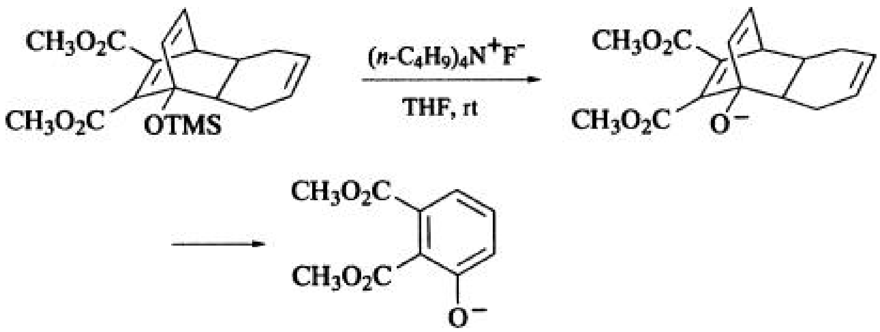
(149)

Formation of carbanion **108** leads to a rapid retro Diels–Alder reaction at 25° (Eq. 150). (142) The placement of an anionic substituent on the latent diene portion of the molecule also accelerates the retro Diels–Alder reaction (Eq. 151). (142) The relatively



108

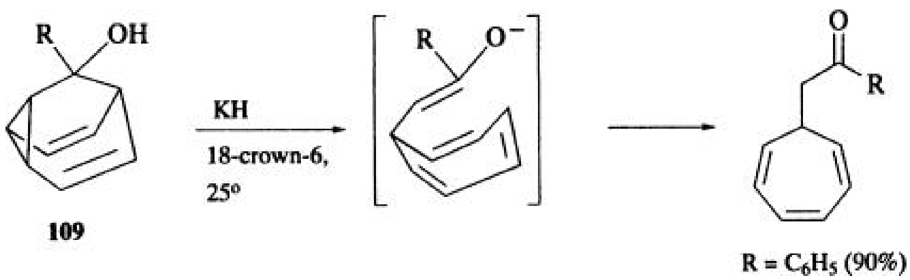
(150)



(151)

mild conditions of the anion-assisted [2 + 4] cycloreversion permit the use of a suitable diene as a protecting group for a double bond during synthesis. (143) The example in Eq. 151 is unusual in that the alkoxide substituent is generated by the cleavage of a trimethylsilyl ether with fluoride ion. An unsuccessful attempt to induce an anion-assisted oxy-Cope reaction by this method is given in Eq. 72.

The anion-assisted reverse intramolecular Diels–Alder reaction of alcohol **109** is successful only when the substituent is a phenyl group (Eq. 151). When the substituent is hydrogen or a methyl group, no reaction occurs, implying that conjugation in the transition state is important. (144)

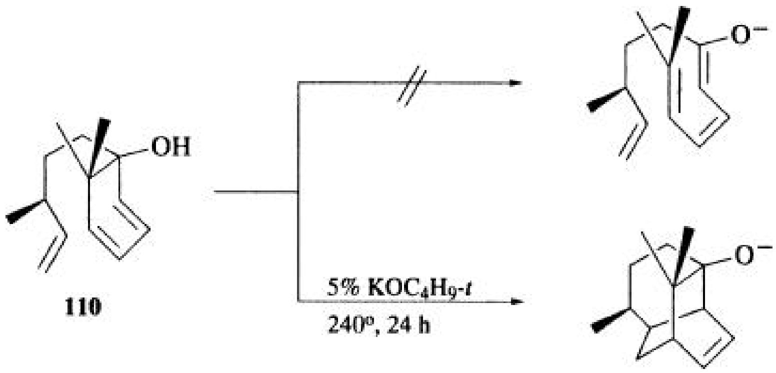


109

(152)

3.6. Electrocyclic [4 p + 2 σ] Ring-Opening Reactions

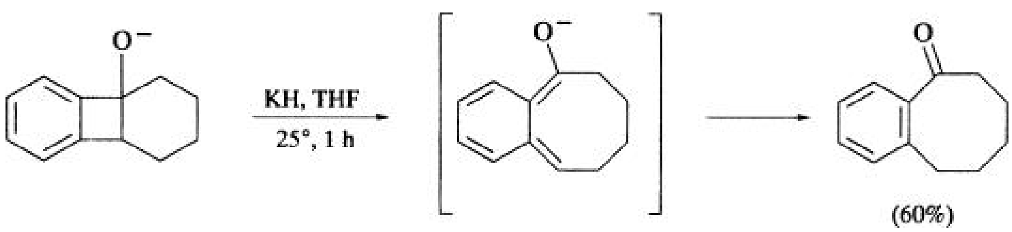
The single known example of an orbital symmetry allowed anion-assisted electrocyclic ring opening is shown in Eq. 25, but there is still the possibility that simple cleavage is responsible for the process. (31) Alcohol **110**, on heating to 240° in the presence of base undergoes an intramolecular Diels–Alder reaction instead of [4 π + 2 σ] ring opening (Eq. 153). (145) Nevertheless, the reaction may be possible in favorable situations.



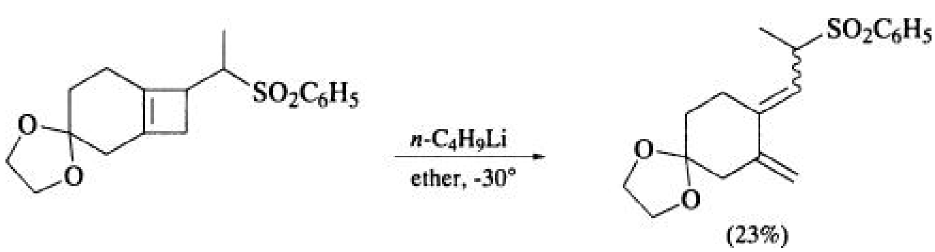
(153)

3.7. Electrocyclic [2 p + 2 σ] Ring-Opening Reactions

The [2 π + 2 σ] ring-opening reaction is more common in strained cyclobutane rings. Examples of acceleration by oxyanions (Eq. 154) (146) and carbanions (Eqs. 26 and 155) 32 are known.



(154)



(155)

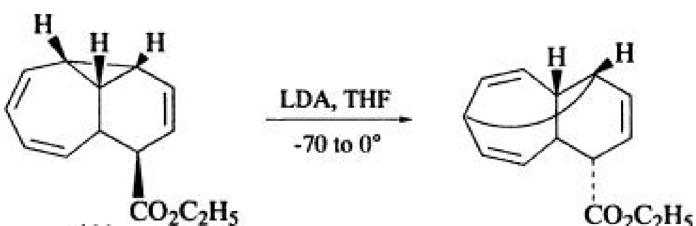
The thermal ring opening of cyclobutene derivatives has been thoroughly studied as to their conrotatory or disrotatory nature, but the anionic version of this reaction has not.

3.8. Miscellaneous Reactions

Several examples of apparent anion-accelerated reactions have appeared which do not fit into any of the previously discussed categories. One reaction involves a nitrogen-centered anion which undergoes a rapid [1,3]-sigmatropic shift (Eq. 156). (147) This observation suggests that amide anion assisted rearrangements may be worthy of investigation.

(156)

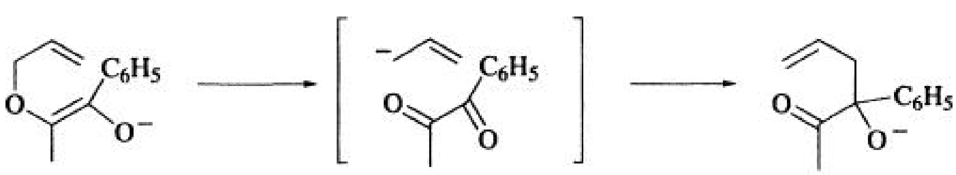
Epimerization of ester **111** is accompanied by a vinylcyclopropane-type [1,3]-sigmatropic shift which is apparently facilitated by the enolate (Eq. 157). (148) This [1,3] shift is an example of an emerging new class of reactions wherein the anionic substituent is vinylogously adjacent to the cleaving C - C bond.



111

(157)

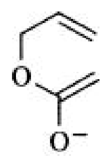
The reaction of Eq. 158 is an example of an anionic oxy-Claisen rearrangement. (149) This process proceeds by a heterolytic cleavage pathway (structure **112**)



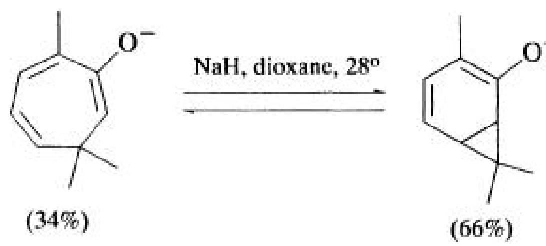
(158)

112

characteristic of the rearrangements discussed in this chapter. The placement of the anionic substituent is different from that in the ester enolate Claisen rearrangement of substrates such as **113**. (6) Anionic substituents may be present in the framework of systems rearranging by other sigmatropic pathways (e.g. Eq. 159) (150) but they do not provide the unique reaction acceleration characteristic of the reactions discussed in this chapter.



113



(159)

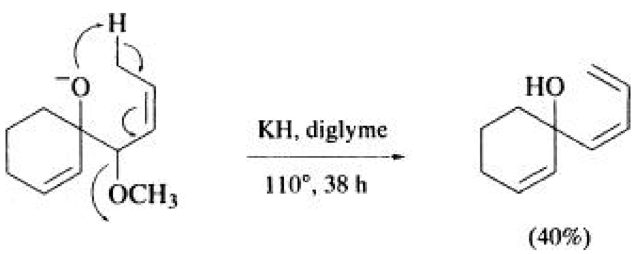
4. Common Side Reactions

Most anion-assisted sigmatropic rearrangements take place in polar aprotic solvents such as tetrahydrofuran and hexamethylphosphoric triamide with alkoxide salts of potassium or sodium. These strongly basic conditions sometimes lead to elimination reactions or double bond isomerization. In addition, a very common side reaction is simple fragmentation at the C - C bond adjacent to the alkoxide substituent. Competition between [3,3]-, [1,3]-, and [1,5]-sigmatropic processes is often observed; the ratios of products can sometimes be varied with reaction conditions.

4.1. Eliminations

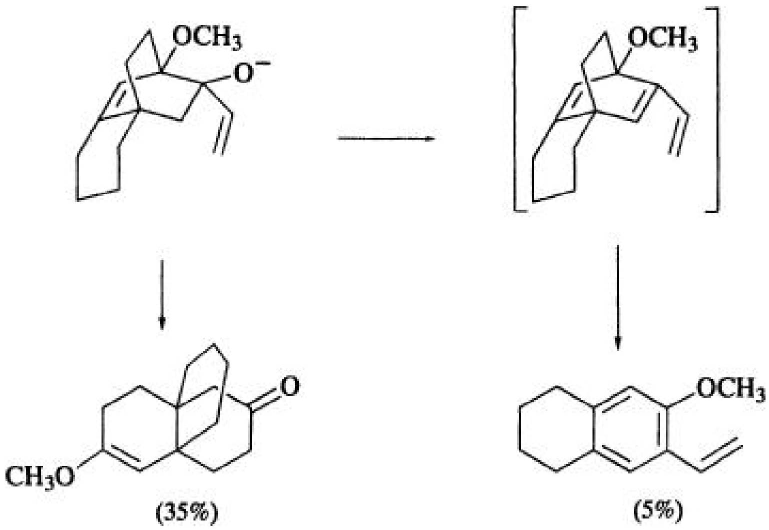
Strongly basic alkoxide solutions at higher temperatures can cleave tetrahydrofuran. (75b) In such cases one must use 1,2-dimethoxyethane (glyme) or bis(2-methoxyethyl) ether (diglyme). The other commonly used solvent, hexamethylphosphoric triamide, is also degraded at higher temperatures.

Elimination is likely to occur when the desired rearrangement is sluggish (Eq. 160). (22)



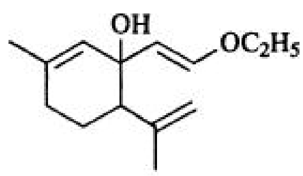
(160)

Another example, involving direct elimination of an alkoxide group followed by a reverse Diels–Alder reaction, is shown in Eq. 161. (62)



(161)

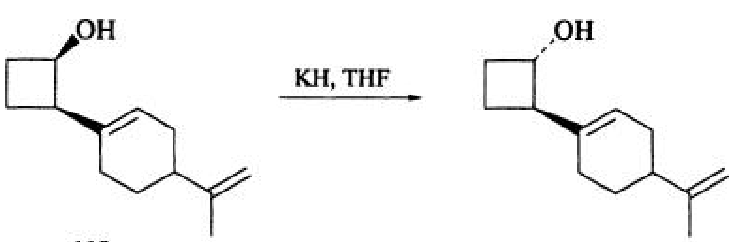
Attempts to carry out the anion-assisted oxy-Cope rearrangement with substrate **114** leads only to decomposition because of elimination of the ethoxy group. (100)



114

4.2. *cis/trans* Isomerizations

Alkoxide-induced *cis/trans* isomerizations, such as that of alcohol **115** (Eq. 162), often occur under the same conditions as a related sigmatropic shift and sometimes precede other rearrangements. (113) Examples are collected in Table XXVI.

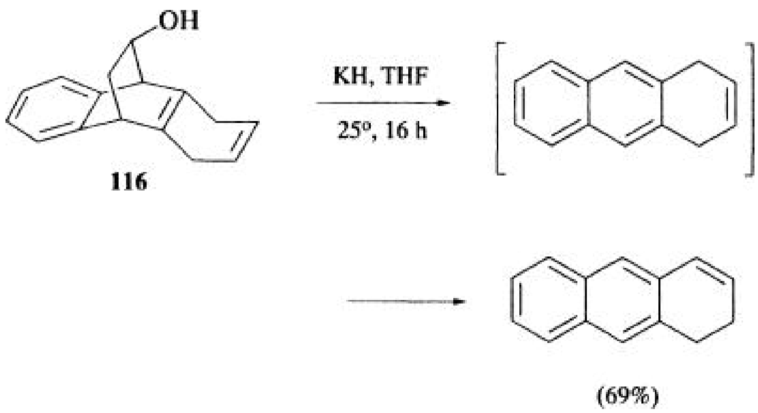


115

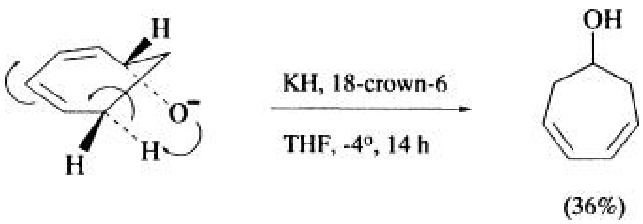
(162)

4.3. Double Bond Isomerizations

A common side reaction is the isomerization of double bonds under the strongly basic reaction conditions. The anion-assisted retro Diels–Alder reaction of alcohol **116** (Eq. 163) leads to increasing amounts of the more stable 1,2-dihydroanthracene at longer reaction times. (140) Isomerizations often appear to occur in an intramolecular sense (Eq. 164). (121) The attempted [3,3]-sigmatropic rearrangement of alcohol **117** leads to ketone **118** by double bond isomerization to the enolate position (Eq. 165). (97)



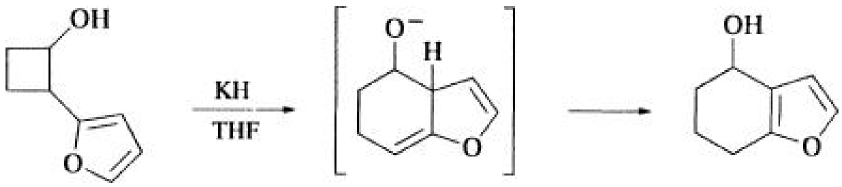
(163)



(164)

(165)

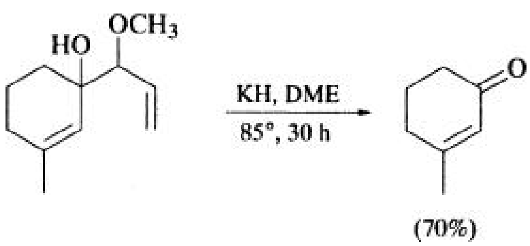
Sometimes double bond isomerization facilitates the overall reaction because it regenerates an aromatic system (Eq. 166). (113)



(166)

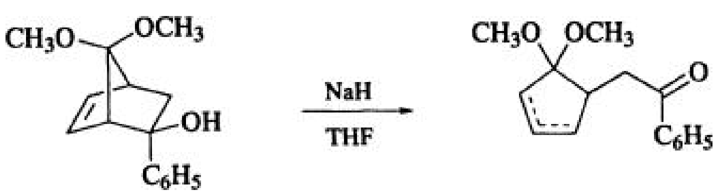
4.4. Fragmentations

The same weakening of the C - C bond in the transition state that causes the rate acceleration in sigmatropic processes frequently leads also to direct fragmentation (Eq. 167). (75b) This problem can often be obviated by using less vigorous conditions,



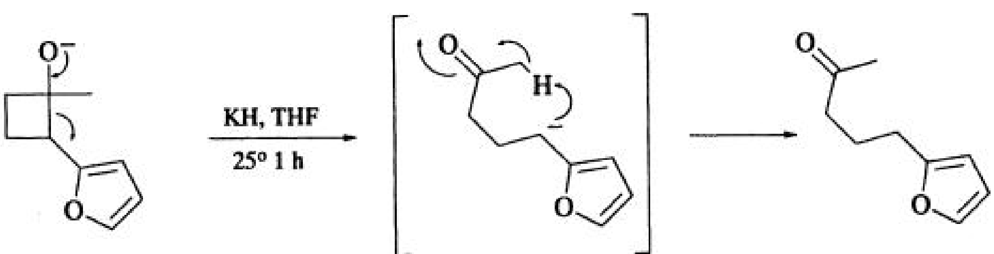
(167)

such as a less highly dissociated counterion (cf. Eq. 104). Fragmentation often results from an unfavorable steric disposition for rearrangement (e.g., Eq. 168) or an



(168)

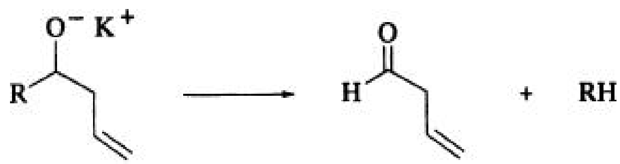
unusually favorable situation for proton transfer. For example, in contrast to the successful [1,3] rearrangement of the parent secondary alcohol (Eq. 166), the tertiary alcohol **119** gives only fragmentation (Eq. 169) perhaps because of intramolecular enolization of the intermediate. (113)



119 (83%)

(169)

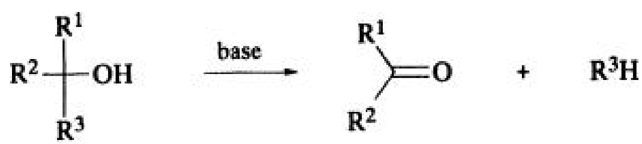
The propensity for fragmentation in compounds **120** decreases in the order R = $C_6H_5CH_2$ > - $C(CH_3)_2C = CH_2$ > - $CH(CH_3)CH = CH_2$ > = $CH_2CH = CH_2$ > - $CH_2C(CH_3) = CH_2$ (Eq. 170). (76)



120

(170)

A comprehensive study of the cleavage of alcohol **121** (Eq. 171) with different bases, solvents, and steric environments is particularly relevant. The previously discussed

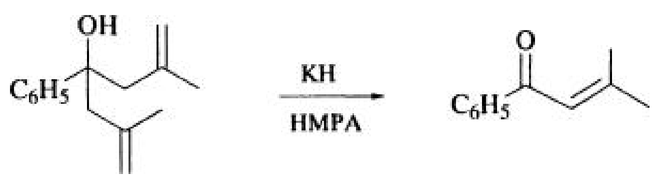


121

(171)

factors that favor increased reaction rates for anion-assisted rearrangements also accelerate fragmentations. These include increased charge density on the alkoxide (K^+ > Na^+ > Li^+) and more polar solvents. (151)

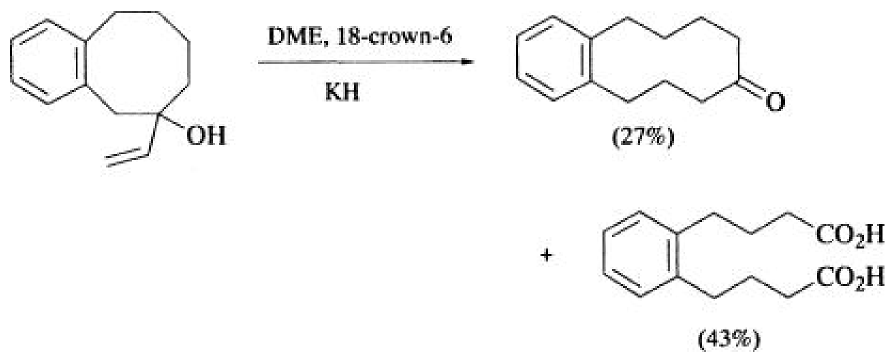
A practical application of anion-induced alkoxide fragmentation involves the cleavage of various diallylcarbinols (Eq. 172). (67) The fragmentation process has been



(172)

used as a synthetic method to prepare α - and β -damascone, β -damascenone, and β-termerone (Eq. 173). (76) The oxidative cleavage shown in Eq. 174 probably involves the reaction of an enolate with molecular oxygen. (123)

(173)



(174)

5. Experimental Conditions

In most reactions, formation of an alkoxide intermediate is required prior to the thermal rearrangement step. Since reaction rates are in the order $K^+ > Na^+ > Li^+$, the formation of potassium salts with potassium hydride is the most important procedure. A detailed paper describing potassium hydride has appeared (152) and a review (153) discusses its applications. Sodium salts are more rarely employed but generally are produced in a similar manner using sodium hydride. Lithium salts are formed most conveniently by reaction of alcohols with *n*-butyllithium. Often, however, lithium alkoxides can be formed in situ by the reaction of an appropriate carbonyl compound with an alkyllithium reagent, thereby generating the substrate as its alkoxide directly. Examples of all of these methods are provided.

5.1. Potassium Hydride

5.1.1.1. Storage and Transfer (152)

Potassium hydride is currently obtained as a dispersion in mineral oil containing 20–35% of the hydride by weight. Although pure potassium hydride is a white powder, most commercial samples are gray, presumably because of traces of unreacted potassium. Potassium hydride reacts slowly with oxygen but can be stored in glass or polyethylene bottles under an inert atmosphere, sealed to prevent exposure to oxygen and moisture.

Transfers of the potassium hydride dispersion may be made quickly in air without difficulty, but for prolonged handling a glove bag (nitrogen or argon) is desirable. Routine transfers are performed directly from the storage container. Two holes just sufficient to accept an 18–19 gauge hypodermic needle are punched in the polyethylene container near the screw cap and can be capped with a small rubber stopper. Through one hole a stream of dry nitrogen is introduced with a short needle, providing a backflush during transfer. It is convenient to put a magnetic stirbar in the container and stir a few minutes to get a homogeneous suspension. The dispersion is transferred using a disposable pipet having a 2–3 mm orifice. The container is then purged with nitrogen, and the holes are capped and sealed with paraffin tape.

Utensils and glassware coated with the potassium hydride dispersion can be cleaned by rinsing with a 10% solution of ethanol in pentane. **CAUTION**! *Under no conditions should the potassium hydride dispersion be exposed to water; it will ignite. Disposal of organic solvents containing even traces of potassium hydride in sinks will produce a fire*.

5.1.1.2. Standardization of Potassium Hydride (152)

A weighed sample of the potassium hydride dispersion (1–2 g) is placed in a flask equipped with a Teflon-covered magnetic stirring bar, condenser, and injection port capped with a rubber septum. The apparatus is purged with nitrogen and connected through traps to a gas-measuring device. The flask is immersed in a water bath and, with stirring, 20 mL of 2-butanol is added, dropwise at first, until hydrogen evolution moderates. The potassium hydride present is determined by a standard gas law calculation; one mole of hydrogen is liberated from each mole of the hydride.

The resulting solution in the flask can be diluted with water and titrated to a phenolphthalein end point. Substantial excesses (>5%) of total base over hydride base (as calculated from the gas evolved) indicate significant hydrolysis of the original potassium hydride sample.

5.1.1.3. Removal of the Oil

The potassium hydride is placed in the apparatus described above, with a bubbler replacing the gas-measuring device. Dry pentane, ether, or similar solvent (5–10 mL/g of dispersion) is added. The mixture is stirred briefly and allowed to settle with occasional tapping; the solvent–oil solution is then removed by syringe. Three such washings remove all but traces of the oil. To facilitate removal of the solvent, an 18–20 gauge flat-tipped needle 20–25 cm long is used. The wash solvent may contain traces of potassium hydride and must be treated with ethanol before disposal. Residual solvent is removed under vacuum or with a stream of nitrogen or argon.

5.1.1.4. Purification of Potassium Hydride with Iodine (42)

Commercial potassium hydride is prepared by reduction of metallic potassium and may contain variable amounts of impurities such as unreacted elemental potassium and its oxidation product potassium superoxide. Such impurities do not necessarily cause problems but can be removed by a simple purification with iodine. This treatment presumably converts elemental potassium into potassium iodide, and potassium superoxide into potassium iodide and oxygen. Commercial potassium hydride (35% suspension in mineral oil) is washed three times with petroleum ether (~4 mL/10 mmol KH) and then resuspended in the desired solvent (THF, DME, ether) at 0.1–1.0 M. The resulting potassium hydride suspension can either be titrated with a solution of iodine in the desired solvent (0.1–0.5 M) until the purple–orange iodine color persists for at least 5 minutes or treated dropwise with a standard quantity of iodine (10 mol %) in the desired solvent. The suspension of potassium hydride and potassium iodide thus generated can be employed in any subsequent reaction.

5.2. Solvents

The most suitable solvents for reactions involving potassium hydride at or below room temperature are ethers, especially tetrahydrofuran, glyme, or diglyme. Potassium Hydride does not dissolve in these solvents. Many reactions of potassium hydride are sluggish in hydrocarbon solvents such as pentane or benzene. Hexamethylphosphoric triamide is stable to potassium hydride but undergoes decomposition at temperatures above 70°. **CAUTION**: *Hexamethylphosphoric triamide has been implicated as a potent animal carcinogen; it must be handled only with good ventilation and while wearing gloves*. Dimethyl sulfoxide is rapidly metalated by potassium hydride and forms the potassium dimsyl anion. Dimethylformamide is reduced by potassium hydride and yields dimethylamine upon hydrolysis.

6. Experimental Procedures

6.1.1.1. cis-2-Hydroxy-5-methylbicyclo[4.4.0]deca-4,7-diene ([1,3]-Sigmatropic Rearrangement of a 2-Vinylcyclobutanol) (112)

A solution of *cis*-8-methyl-8-vinylbicyclo[4.2.0]oct-2-en-7-one (0.162 g, 1 mmol) in 8 mL of THF was treated with Li(*s* – Bu)$_3$ BH solution (1.0 M in THF, 1.15 mmol) for 15 minutes. Methyllithium solution (1.16 M in ether, 1.0 mL, 1.16 mol) and 5 mL of HMPA were added and the mixture was heated at 70° for 15 hours. The mixture was cooled to room temperature and treated with 5 mL of 15% NaOH and 3 mL of 30% H_2O_2 at 25° for 15 hours. The mixture was diluted with ether, the organic layer was washed with water and saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated to afford 0.191 g of a pale yellow oil. Column chromatography on silica gel (elution with ether–hexane) gave 0.137 g (83%) of *cis*-2-hydroxy-5-methylbicyclo[4.4.0]deca-4,7-diene (85:15 mixture of epimers) as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 5.66–5.77 (m, 2H), 5.21–5.26 (m, 1H), 3.86 (dd, *J* = 6.7, 12.9 Hz, 1H), 2.79 (m, 1H), 1.73 (m, 3H), 1.47–2.14 (m, 7H); IR (film) 3340, 3020, 2920, 2830, 1665, 1645, 1430, 1370, 1030, 890, 855, 795, 750, 725 cm^{-1}. HRMS, m/z calcd for $C_{11}H_{16}O$, 164.1201; found, 164.1192.

6.1.1.2. Bicyclo[5.3.1]undec-1(11)-en-4-one ([3,3]-Sigmatropic Rearrangement of a 1,2-Divinylcyclobutanol) (24)

A mixture of diastereomeric 1-ethenylspiro[3.5]non-5-en-1-ols (0.473 g, 2.88 mmol) in 10 mL of dry THF was added to a stirred suspension of hexane-washed potassium hydride (0.483 g of 24% KH in oil, 2.90 mmol) in 30 mL of dry THF at 25° under nitrogen. After 10 minutes at 25°, the reaction was quenched with 1 mL of saturated aqueous NH_4Cl , filtered through a glass wool plug, dried ($MgSO_4$), and concentrated under vacuum. The residue was purified by flash chromatography (18 g of silica gel, 5% ethyl acetate/hexane) to afford 0.379 g (80%) of the title compound as an oil. ^{1}H NMR (CCl_4) δ 5.10 (br, s, 1H), 1.0–3.0 (m, 15H); IR (CCl_4) 2940 (s), 1700, 1450 (m), 1080 (m), 900 (m) cm^{-1}. MS, m/z 164 (M^+), 146, 136, 107, 94 (base), 79, 57, 43.

6.1.1.3. 6,10-Dimethyl-6-trimethylsilyloxyundeca-1,3,9-triene ([1,3]-Sigmatropic Rearrangement of a 3-Alkoxyalkyl-1,4-diene) (107)

n-Butyllithium solution was added dropwise to a cold (0°) solution of 4,8-dimethyl-3-vinylnona-1,7-dien-4-ol (9.70 g, 0.05 mol) and triphenylmethane (0.150 g) in THF (300 mL) over 15 minutes until a faint pink color was observed (21 mL of 2.4 M *n*-butyllithium in hexane was required). The mixture was heated at reflux for 2.5 hours, then chlorotrimethyl-silane (8.15 g, 0.075 mol) was added, and the mixture was heated for an additional 2.5 hours. Workup and distillation (130°, 0.3 mm) gave 6.5 g (98%) of 6,10-dimethyl-6-trimethylsilyloxyundeca-1,3,9-triene. ^{1}H NMR ($CDCl_3$) δ 6.34 (dt, *J* = 16.7, 10.3 Hz, 1H), 6.07 (dd, *J* = 15.2, 10.3 Hz, 1H), 5.07 (dt, *J* = 15.1, 7.5 Hz, 1H), 4.96–6.12 (m, 2H), 2.27 (d, J = 7.5 Hz, 2H), 2.06 (dt, J = 8.5, 7.5 Hz, 2H), 1.70 (s, 3H), 1.63 (s, 3H), 1.41–1.51 (m, 2H), 1.22 (s, 3H), 0.14 (s, 9H); IR (film) 2950, 1650, 1460, 1360 cm^{-1}. MS, m/z 201, 200, 199, 131, 73, 69.

6.1.1.4. cis-(4-Vinyl-3-cyclopentenyl)acetaldehyde ([3,3]-Sigmatropic Rearrangement Leading to Contraction of a Medium-Sized Ring) 94

Potassium hydride (15.0 g of a 23.6% suspension, 88 mmol) was placed in a 250-mL, round-bottomed flask, blanketed with nitrogen, and washed free of oil with anhydrous ether (2 × 50 mL). Additional dry ether (75 mL) was added and the slurry was stirred at 0° while cyclonona-2,4,7-trienol (10.0 g, 73.5 mmol) dissolved in 75 mL of ether was added dropwise. After the addition, the solution was allowed to warm to room temperature and stirred for 4 hours. The reddish-brown mixture was rapidly poured into a stirred mixture of 10% aqueous NH_4Cl (100 mL) and ice (50 g). The organic phase was separated, washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried, and concentrated to yield 9.9 g (99%) of *cis*-(4-vinyl-3-cyclopentenyl)acetaldehyde. ^{1}H NMR ($CDCl_3$) δ 9.78 (t, J = 1 Hz, 1H), 6.0–5.35 (m, 2H), 3.5–2.0 (m, 6H); IR (film) 1720, 1620 cm^{-1}. HRMS, calcd for $C_9H_{12}O$ 136.0888; found 136.0892.

6.1.1.5. Anionic Rearrangement of Cyclohepta-2,4-dien-1-ol ([1,5]-Hydrogen Shift) (121)

A slurry of KH (from 500 mg of a 40% dispersion, 5 mmol) was prepared in dry THF (25 mL) under nitrogen, cooled to –5°, and cyclohepta-2,4-dien-1-ol (150 mg, 1.36 mmol) in THF (2 mL) was added. The mixture was stirred for 14 hours at –5°. Aqueous NH_4Cl solution was introduced slowly to quench the excess KH, the aqueous layer was extracted with ether (2 × 50 mL), and the combined ether extracts were washed with water and brine prior to drying. Solvent removal followed by distillation yielded 135 mg (90%) of a mixture of cyclohepten-3-one and cyclohepta-3,5-dienol in a ratio of 3:2. Purification was accomplished by VPC on a 4-ft × 0.25-in. 10% SE-30 column at 70°. Cyclohepten-3-one: ^{1}H NMR ($CDCl_3$) δ 6.0–5.5 (m, 2H), 3.1–3.0 (m, 2H), 2.4–1.4 (m, 6H); IR (film) 3020, 2950, 2860, 1710, 1300, 1215, 1120, 955, 930, 890, 680 cm^{-1}. Cyclohepta-3,5-dienol: ^{1}H NMR (CCl_4) δ 6.0–5.5 (m, 4H), 4.4–4.0 (m, 1H), 2.7–2.38 (m, 4H), 2.0 (br s, 1H).

6.1.1.6. 3,4,4a α ,7,8,8a α-Hexahydronaphthalen-2(1H)-one (Cope Rearrangement of a Bicyclic Vinylcarbinol) (154)

Postassium hydride dispersion (17.8 g of 22% KH, 97.8 mmol) was washed to remove the oil. A solution of a 2:1 mixture of *endo, exo*-2-vinyl-2-hydroxybicyclo[2.2.2]oct-5-enes (7.35 g, 48.9 mmol) in dry THF (200 mL) was added, and the resulting alkoxide solution was heated at reflux for 18 hours. The mixture was cooled and quenched with ethanol (20 mL) and water. Isolation under standard conditions via ether extraction gave 7.19 g of a mixture of unreacted *exo*-2-vinyl-2-hydroxybicyclo[2.2.2]oct-5-ene and the product as a brown oil. Chromatographic separation on neutral alumina (180 g, activity III) with 30% ether–hexane gave 4.82 g (98% based on the starting *cis* alcohol) of pure 3,4,4a α ,7,8,8a α -hexahydronaphthalen-2(1*H*)-one as a colorless oil. ^{1}H NMR δ 5.70 (br s, 2H), 2.7–1.3 (br m, 12H); IR (film) 3020, 1700, 1640 cm^{-1}. HRMS calcd for $C_{10}H_{14}O$, 150.104; found 150.106.

6.1.1.7. 6-Methylcyclodec-5-enone (Cope Rearrangement of a 1,2-Divinylcycloalkanol) 62b

Potassium hydride (24% dispersion in oil, 131 mg, 0.787 mmol) was placed in a flask fitted with a septum, the oil was removed as described above, and then THF (5 mL) was added. 1,2-Diethenyl-2-methylcyclohexanol (109 mg, 0.656 mmol) was added and the mixture stirred at room temperature until the evolution of hydrogen ceased. The flask was then blanketed with nitrogen, a condenser was added, and the mixture was refluxed for 15 minutes. The reaction mixture was cooled and worked up in a standard manner. Evaporation of the solvent and Kugelrohr distillation of the residue (bp 90° at 0.05 mm) gave 104 mg (95%) of 6-methylcyclodec-5-enone. VPC analysis (6 ft 10% DEGS on 80–100 mesh Chromosorb W) showed an *E:Z* double bond ratio of 1:8.6. ^{1}H NMR ($CDCl_3$) δ5.08–5.21 (m, 0.1H), 4.89–5.05 (m, 0.9H), 2.27–2.51 m, 2H), 1.45–2.21 (m, 15H); IR (film) 1704 cm^{-1}. HRMS calcd for $C_{11}H_{18}O$ 166.1357; found 166.1356.

6.1.1.8. 3-[3-Methoxy-1-methyl-(E)-2-propenyl]cyclohexanone (Cope Rearrangement of an Allylcyloalkanol) (22)

To a suspension of 2.0 g (50 mmol) of oil-free potassium hydride (from 8.9 g of a 22% dispersion) in 110 mL of diglyme under an argon atmosphere was added 3.0 g (17 mmol) of 1-[1-methoxy-(*E*)-2-butenyl]-2-cyclohexen-1-ol. The solution was heated at 100° for 37.5 hours. The resulting dark brown solution was added to 50 mL of saturated ammonium chloride solution and the aqueous phase was extracted twice with pentane. The combined organic extracts were washed, dried, and concentrated to give an orange oil. Bulb-to-bulb distillation (110° at 0.05 mm) gave 2.3 g (77%) of 3-[3-methoxy-1-methyl-(*E,Z*)-2-propenyl]cyclohexanone as a 60:40 mixture of *E* and *Z* isomers. ^{1}H NMR ($CDCl_3$) δ 6.2 (d, 0.6H, *trans*), 5.88 (d, 0.4H, *cis*), 4.53 (m, 0.6H, *trans*), 4.11 (m, 0.4H, *cis*), 3.51 (s, 1.2H), 3.47 (s, 1.8H), 2.65–1.12 (m, 10H), 0.99 (d, 3H), 0.94 (d, 3H); IR (film) 3020, 2940, 1705, 1650, 1450, 1375, 1100, 940, 760 cm^{-1}.

6.1.1.9. Retro Diels–Alder Reaction of 11-Hydroxy-9,10-dihydro-9,10-ethanoanthracene ([2 + 4] Cycloreversion Reaction) (140)

A mixture of 0.100 g (0.45 mmol) of 11-hydroxy-9,10-dihydro-9,10-ethanoanthracene and 0.020 g (0.50 mmol) of potassium hydride was stirred at room temperature in 7 mL of anhydrous THF and 3 mL of HMPA for 66 hours. Water (~50 mL) was added and the mixture was extracted with petroleum ether. Concentration and filtration through silica gel gave 0.049 g (60%) of anthracene, identified by comparison with an authentic sample.

6.1.1.10. Fragmentation of 2-Methylbicyclo[2.2.2]oct-5-en-2-ol (Fragmentation Reaction) (138)

2-Methylbicyclo[2.2.2]oct-5-en-2-ol (10 mmol) in HMPA (5 mmol) was added dropwise to a stirred slurry of potassium hydride (24% in oil, 11 mmol) at 10° under nitrogen. After 20 minutes the mixture was heated at 120° for 2 hours. After cooling, the mixture was poured into an excess of cold saturated NH_4Cl solution. Ether extraction and usual product isolation gave an oil that was distilled (100–110° at 0.01 mm) to give 1-(3¢-cyclohexenyl)-2-propanone (68%). ^{1}H NMR δ 5.65 (m, 2H), 2.39 (d, *J* = 7 Hz, 2H), 2.15 (s, 3H), 2.08 (m, 3H), 1.27 (m, 1H), 1.07 (m, 3H); IR 3030, 1710, 1360, 1160, 915, 730, 654 cm^{-1}. MS (m/z) 138, 95, 81, 80, 79, 67, 59.

6.1.1.11. (2Z,6E)-3,7-Dimethyl-9-(1-methylethylidenyl)-2,6-cyclodecadien-1-one (Solvent-Induced [3,3]-Sigmatropic Rearrangement) (100)

A solution of 3-methyl-1 α -(3-methyl-1,2-butadienyl)-6 β -(1-methylethenyl)-2-cyclohex-1 β -enol (544 mg) in 6 mL of 1-methyl-2-pyrrolidinone was heated at 120–130° for ~10 hours under argon. After cooling, the mixture was poured into water and extracted with ether. Usual isolation gave a mixture of starting material, product, and a bicyclic byproduct in a ratio of 3:2:2. Column chromatography on silica gel (hexane–ethyl acetate mixture) gave 139 mg (26%) of product. ^{1}H NMR (CCl_4) δ 5.77 (br s, 1H), 4.94 (t, *J* = 8 Hz, 9H), 1.77 (br s, 9H), 1.35 (s, 3H); IR (film) 1680, 1633, 1210, 1085, 992 cm^{-1}. MS (m/z) 218, 200, 185. HRMS calcd for $C_{15}H_{22}O$ 218.1666; found 218.1669.

6.1.1.12. Cyclotetradeca-3,5,7-trien-1-one ([5,5]-Sigmatropic Rearrangement) (102)

To a suspension of potassium hydride (404 mg, 2.2 mmol, 22% dispersion) at 0° was added dropwise a solution of (*E,E*)-1,2-bis(1-buta-1,3-dienyl)cyclohexanol (174.6 mg, 0.855 mmol) in THF. The mixture was allowed to warm to room temperature for 1 hour. It was then recooled to 0°, saturated NH_4Cl solution was added, and the aqueous phase was extracted with dichloromethane. The combined extracts were dried and concentrated, and the residue was chromatographed on silica gel, eluting with 97% ether–pentane, to give 157 mg (90%) of a faintly yellow solid (mp 50.5 – 51.5°). ^{1}H NMR ($CDCl_3$) δ 6.2–4.75 (m, 6H), 3.1–2.75 (br d, 2H), 2.7–2.3 (m, 2H), 2.3–1.8 (m, 6H), 1.75–1.25 (m, 4H); IR (CCl_4) 1705, 1650, 1440, 1430, 1100, 990, 975 cm^{-1}. HRMS calcd for $C_{14}H_{20}O$ 204.1541; found 204.1513.

6.1.1.13. 11,11-Dimethylbicyclo[6.2.1]undec-1-en-6-one (Cope Rearrangement of a Bicyclic Vinylcarbinol) (155)

A suspension of iodine-purified potassium hydride was prepared as follows. A potassium hydride dispersion (25% in mineral oil, 14.8 mmol) was washed with petroleum ether (2 × 2 mL) and suspended in dry THF (5 mL). The magnetically stirred suspension was treated with a 10 mol% solution of iodine in THF until the brown-orange color persisted for 5 minutes. Then 3.92 g (14.8 mmol) of 18-crown-6 was added, followed by 567 mg (2.97 mmol) of 1,2-divinyl-7,7-dimethyl-*exo*-norbornan-2-ol in THF (2 mL). The mixture was stirred at room temperature for 15 minutes, cooled to –78°, and quenched with absolute ethanol (1 mL)/saturated ammonium chloride solution (15 mL). The product was extracted into ether and the ether layers were washed with brine, dried, and concentrated. Purification by chromatography on silica gel gave 490 mg (86%) of 11,11-dimethylbicyclo[6.2.1]undec-1-en-6-one as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 4.91–4.87 (m, 1H), 2.62–2.54 (m, 2H), 2.35–1.93 (series of m, 8H), 1.89–1.74 (m, 2H), 1.69–1.60 (m, 1H), 1.11 (s, 3H), 1.05 (s, 3H). MS calcd: 192.1514, found 192.1507. Anal. calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.17; H, 10.51.

6.1.1.14. endo-7-Hydroxymethyl-3,7-dimethyl-cis-bicyclo[4.3.0]non-8-en-4-one (Cope Rearrangement of a Bicyclic Vinylcarbinol) (156)

A solution of *endo*-2-isopropenyl-7-*anti*-methyl-7-hydroxymethylbicyclo[2.2.1]-hept-5-en-2-ol (3.8 g, 19.6 mmol) in THF (10 mL) was added to a rapidly stirred suspension of potassium hydride (1.9 g, 47.5 mmol) in THF (30 mL). The mixture was stirred at room temperature for 2 hours and then quenched with methanol (1 mL) and concentrated. The residue was diluted with water and extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine, dried, and concentrated under reduced pressure. Purification of the crude product on silica gel gave 3.58 g (94%) of pure *endo*-7-hydroxymethyl-3,7-dimethyl-*cis*-bicyclo[4.3.0]non-8-en-4-one as a colorless oil. ^{1}H NMR ($CDCl_3$) δ 5.75 (m, 1H), 5.48 (m, 1H), 3.45 (s, 2H), 3.04 (m, 1H), 2.67 (m, 1H), 2.38–2.03 (m, 5H), 1.5 (m, 1H), 1.08, (s, 4.5H), 1.05 (s, 1.5H); IR (neat) 3600–3300, 1710 cm^{-1}. MS calcd 194.1307, found 194.1280.

6.1.1.15. 4-(2-Propyl)-5(E)-cyclodecenone (Cope Rearrangement of a Divinylcycloalkanol) (42)

A potassium hydride/mineral oil dispersion (2.61 mmol) was washed with pentane (3 × 1 mL) and suspended in THF (2 mL). 18-Crown-6 (690 mg, 2.61 mmol) and 1-ethenyl-2-[3-methyl-(1-butenyl)]cyclohexan-1-ol (102 mg, 0.522 mmol) dissolved in THF (1.5 mL) were added and the mixture was refluxed for 2 hours. The mixture was then cooled to –78° and quenched with absolute ethanol. The resulting slurry was partitioned between petroleum ether (5 mL)/saturated ammonium chloride solution (5 mL) and the organic layer was washed with brine, dried, and concentrated. Chromatography on silica gel gave 85.5 mg of 4-(2-propyl)-5(*E*)-cyclodecenone as a waxy solid (mp ~28°). ^{1}H NMR ($CDCl_3$) δ 5.30 (ddd, *J* = 14.7, 11.0, 3.7 Hz, 1H), 4.94 (dd, *J* = 14.7, 10.6 Hz, 1H), 2.50 (dd, *J* = 16.1, 9.9 Hz, 1H), 2.43–2.12 (m, 4H), 2.04 (q, *J* = 12.6 Hz, 1H), 1.93 (m, 2H), 1.63 (m, 2H), 1.48 (sextet, *J* = 6.7 Hz, 1H), 1.32 (q, *J* = 13.4 Hz, 1H), 0.86 (d, *J* = 6.7 Hz, 3H). MS (CI), m/z 195 (M + 1). Anal. calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.20; H, 11.44.

6.1.1.16. 4-(tert-Butyldimethylsilyloxymethyl)-1,1-dimethoxy-3a α ,4 α ,5,7a α -tetrahydro-7H-inden-6-one (Cope Rearrangement of a Bicyclic Vinylcarbinol) (59)

Sodium hydride was washed with anhydrous hexane and suspended in THF (100 mL). A solution of *endo*-2-(*tert*-butyldimethylsilyloxy)prop-1-enyl-*exo*-2-hydroxy-7,7-dimethoxybicyclo[2.2.1]hept-5-ene (2.5 g, 7.4 mmol) in THF (50 mL) was added dropwise to the suspension at 0°. The mixture was heated at reflux for 90 minutes, then cooled to 0°, quenched with water, and extracted with ether. The organic phases were washed with water until neutral, dried, and concentrated. Recrystallization gave 2.0 g (80%) of a white solid, mp 72–73°. ^{1}H NMR ($CDCl_3$) δ 6.04 (br s, 2H), 3.53 (d, *J* = 6.92 Hz, 2H), 3.35 (m, 1H), 3.23 (s, 3H), 3.20 (s, 3H), 2.83 (m, 1H), 2.65–1.65 (m, 5H), 0.89 (s, 9H), 0.05 (s, 6H); IR (neat) 2950–2650, 1705, 1600, 1440, 1390, 1320, 1320, 1230, 1170, 1130, 1020, 960, 900, 820, 750 cm^{-1}. MS calcd: 340.2070; found 340.2071.

7. Tabular Survey

The tables include examples of anion-assisted sigmatropic rearrangements that have appeared in the literature up to the end of 1989. The tables are arranged in the same order as the text discussion. Entries in each table are in the order of increasing number of carbon atoms, although some exceptions occur when a single structure covers a series with different R groups. The symbol (–) indicates that no yield was reported.

Abbreviations used in the tables are as follows:

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane
[2.2.2]-cryptand	4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane
diglyme	diethylene glycol dimethyl ether
DME	1,2-dimethoxyethane
DMSO	dimethyl sulfoxide
ether	diethyl ether
HMPA	hexamethylphosphoric triamide
MCPBA	*m*-chloroperbenzoic acid
NMP	*N*-methylpyrrolidinone
TBDMS	*tert*-butyldimethylsilyl
TMEDA	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
THF	tetrahydrofuran
THP	tetrahydropyranyl
TMS	trimethylsilyl
triglyme	triethylene glycol dimethyl ether

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols

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Table II. Cope Rearrangements of Bicyclic Vinylcarbinols

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Table III. Cope Rearrangements of Allylcycloalkanols

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Table IV. Cope Rearrangements of 1,2-Divinylcyclobutanols

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Table V. Cope Rearrangements in Open-Chain Systems

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Table VI. Cope Rearrangements of 3-Methylene-1-vinylcycloalkanols

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Table VII. Cope Rearrangements that Contract Medium-Sized Rings

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Table VIII. Substrates that Undergo both [1,3] and [3,3] Rearrangements

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Table IX. Cope Rearrangements that Involve Aromatic Bonds

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Table X. [5,5]-Sigmatropic Rearrangements

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Table XI. [1,3]-Sigmatropic Rearrangements of Allylcarbinols

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Table XII. [1,3]-Sigmatropic Rearrangements of 3-Alkoxyalkyl-1,4-dienes

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Table XIII. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclopropanols

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Table XIV. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclobutanols

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Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted-2-Alkenols

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Table XVI. [1,3]-Sigmatropic Rearrangements in Macrocyclic Systems

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Table XVII. [1,3]-Sigmatropic Rearrangements of Bridged Bicyclic Carbinols

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Table XVIII. [1,3]-Sigmatropic Rearrangements of 1,1-Dialkoxy-Substituted Systems

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Table XIX. [1,5]-Sigmatropic Shifts

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Table XX. [2 + 2] Cycloreversion Reactions

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Table XXI. [2 + 4] Cycloreversions

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Table XXII. Electrocyclic [4 p + 2 σ] Ring Opening Reactions

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Table XXIII. Electrocyclic [2 p + 2 σ] Ring Opening Reactions

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Table XXIV. Solvent-Induced [3,3]-Sigmatropic Rearrangements

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Table XXV. Fragmentation Reactions

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Table XXVI. *cis/trans* Isomerizations

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Table XXVII. Miscellaneous Reactions

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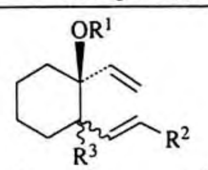
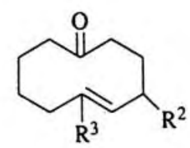
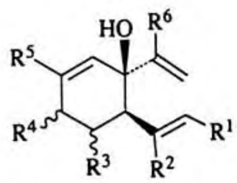
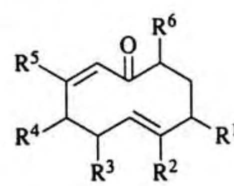
Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols





Carbon No.	R^1	R^2	R^3	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}	H	CH_3	H	KH, THF, 18-crown-6	(—)	48
	H	H	CH_3	KH, THF, reflux	(99)	32b
C_{13}	H	i-C_3H_5	H	KH, THF	(85)	42
	H	$COCH_3$	CH_3	KH, DME,	(50)[a]	45
C_{14}	TMS	CH_3	H	KH, THF	(82)[b]	48
C_{15}	H	$CO_2C_3H_5$-c	CH_3	KH, DME,	(50)[a]	45
C_{16}	H	n-C_6H_{13}	H	KH, THF,18-crown-6	(—)	48





Carbon No.	R^1	R^2	R^3	R^4	R^5	R^6	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}	H	CH_3	H	H	CH_3	H	KH, THF, 18-crown-6 , 25°, 18 h	(75)	34
C_{13}	i-C_3H_7	H	H	H	H	H	KH (10% I_2-treated)[c], THF, 18-crown-6	(70-80)	42
C_{14}	H	CH_3	H	CH_2OCH_3	CH_3	H	KH, THF, reflux, 18-crown-6	(67)	51, 33
C_{15}	H	CH_3	H	H	CH_3	i-C_3H_7	KH, THF, 18-crown-6	(73)	34
C_{19}	i-C_3H_7	CH_3	$CH_2OCH(CH_3)OC_2H_5$	H	H	H	KH, 18-crown-6, 70°, 1 h	(57)[d]	36
C_{20}	i-C_3H_7	CH_3	CH_2OTHP	H	H	H	KH, THF, 18-crown-6	(50)[d]	49

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

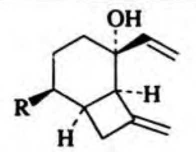
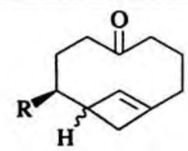
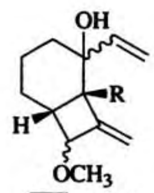
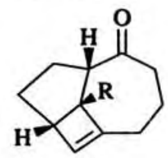
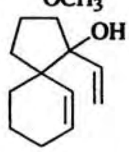
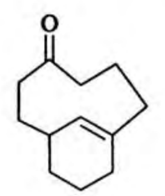
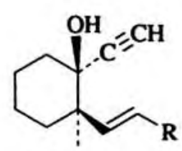
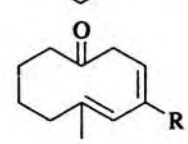
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				
C_{11}	R = H	KH, THF, 18-crown-6, 25°, 2 h	(71)	32c
C_{14}	R = i-C_3H_7	KH, THF, 18-crown-6 (5 eq), 60°, 25 min	(75)	50
C_{12}		KH, 18-crown-6, THF, reflux	 R = H (60)[e] R = CH_3 (40)[e]	157
		KH, THF, reflux, 4 h	 (83)	35
C_{13}		NaH, DME		47
	R = $COCH_3$		(40)	
	R = CO_2CH_3		(45)	

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

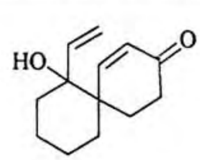
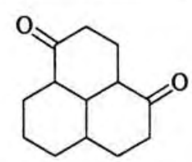
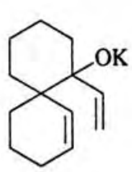
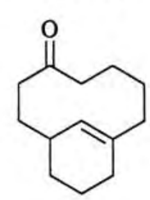
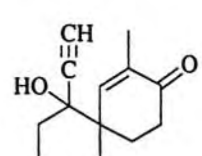
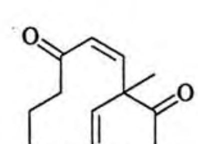
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		4% KOH, H_2O, reflux	 (50)[f]	44
		THF, reflux, 4 h	 (79)	35
C_{14}		KH, DME, 0°	 (67)	89

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

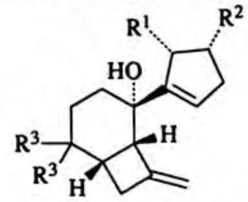
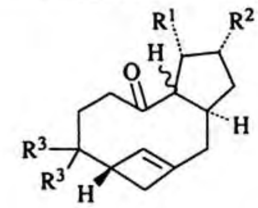
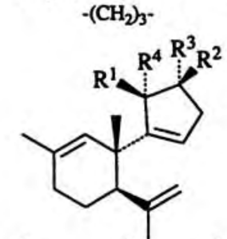
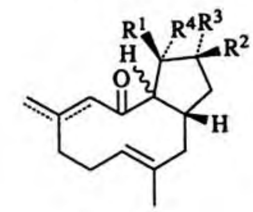
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				158
	R^1 / R^2 / R^3			
C_{17}	i-C_3H_7 / H / H	KH,THF	(95)	
	-$(CH_2)_3$- / H	KH, 18-crown-6, THF	(88)	
	i-C_3H_7 / H / H	$KN(TMS)_2$, THF	(67)	
C_{18}	i-C_3H_7 / H / CH_3	KH,THF	(79)	
	i-C_3H_7 / H / CH_3	$KN(TMS)_2$, THF	(34)[g]	
	-$(CH_2)_3$- / CH_3	KH, 18-crown-6, THF	(88)	
		KH, (I_2-pretreated), 18-crown-6, THF, reflux		43
	R^1 / R^2 / R^3 / R^4			
C_{17}	H / H / -$(CH_2)_2$-		(82)	
	-$(CH_2)_2$- / H / H		(74)	
C_{18}	C_2H_5 / H / CH_3 / H		(82)	
	C_2H_5 / CH_3 / H / H		(74)	
	i-(C_3H_7) / H / H / H		(81)	
	H / H / -$(CH_2)_3$-		(69)	
	-$(CH_2)_3$- / H / H		(65)	

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

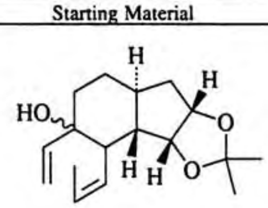
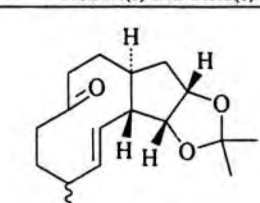
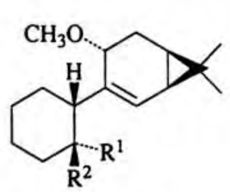
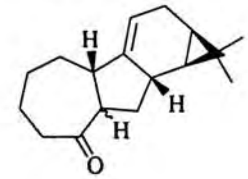
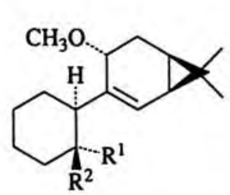
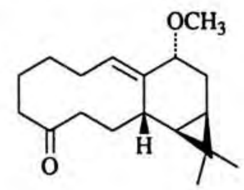
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
C_{17}		KH, THF, $(n$-$C_4H_9)_4N^+I^-$, 12 h	 (74)	20
C_{18}		KH, THF, 18-crown-6, heat		159
	R^1 / R^2			
	OH / CH=CH_2		(71)[h]	
	CH=CH_2 / OH		(0)	
		KH, THF, 18-crown-6, heat		159
	R^1 / R^2			
	OH / CH=CH_2		(36)[i]	
	CH=CH_2 / OH		(67)	

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

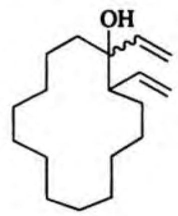
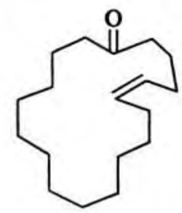
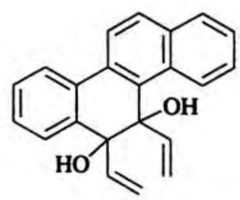
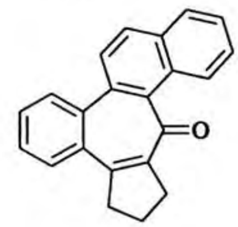
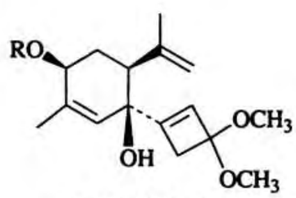
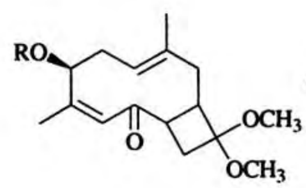
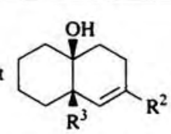
Carbon No.	Starting Material	Reaction Conditions	Product (s) and Yield(s) (%)	Refs.
C_{18}		KH, THF	 (78)	37
C_{22}		KH (2 eq), THF, reflux 12 h	 (40)[j]	46
C_{24}	 R = $CH_2OCH_2C_6H_5$	$KN(TMS)_2$, DME, 85°, 14 h	 (90)	38

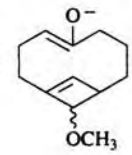
Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

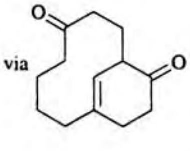
[a] The product  was formed by subsequent transannular cyclization.

[b] The reaction proceeded via in situ cleavage of the TMS ether to a potassium salt.

[c] No product was obtained when untreated KH was used.

[d] The yield is that of the α-hydroxyketone obtained by treatment of the initial enolate with chlorotrimethylsilane followed by MCPBA.

[e] The reaction proceeded via transannular S_N2' cyclization of 

[f] The product is formed via 

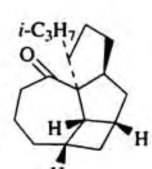
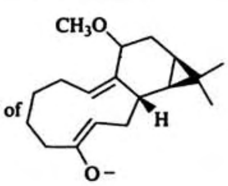
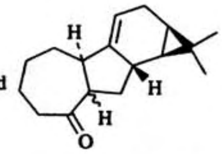
[g] In addition,  was formed in 39% yield by a transannular cyclization.

Table I. Cope Rearrangements of 1,2-Divinylcycloalkanols (*Continued*)

[h] The product was formed via transannular cyclization of 

[i] Formation of compound  in 35% yield was observed.

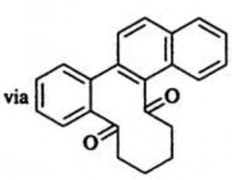
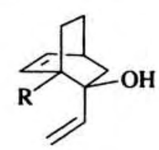
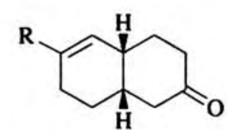
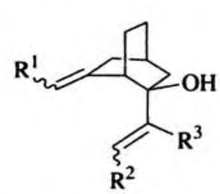
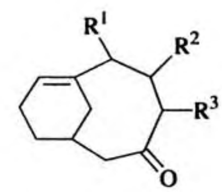
[j] The reaction proceeded via 

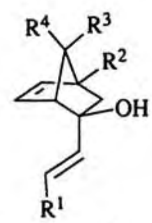
Table II. Cope Rearrangements of Bicyclic Vinylcarbinols

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				
C_{10}	R = H	KH, THF, 65°, several min	(98)	5, 11
	R = H	KH, 18-crown-6, DME, 16 h	(—)	61
	R = H	NaH, THF, 65°, several h	(—)	5, 11
C_{11}	R = OCH_3	KH, THF, 25°, 20 h	(—)	5
				52

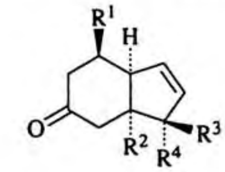
Carbon No.	R^1	R^2	R^3	Product(s) and Yield(s) (%)
	H	H	H	(70-85)
C_{12}	H	H	CH_3	(—)
	CH_3	H	H	(—)

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.

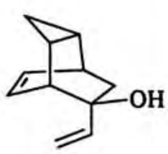


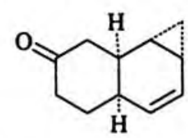
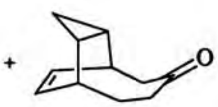
KH, THF, 25°, 10 h



Carbon No.	R^1	R^2	R^3	R^4	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9	H	H	H	H	KH, THF, 65°, 20 min	(70)	160
C_{11}	CH_3	H	H	CH_3	KH	(92)	60
	H	H	OCH_3	OCH_3	KH, THF, 25°	(72)	54
	H	H	OCH_3	OCH_3	Na, THF, 65°	(—)	54
	H	CH_3	CH_2OH	H	KH, THF, 25°	(82)	55a
C_{13}	H	CH_3	$CH(OCH_3)_2$	H	NaH, benzene, reflux	(93)	55a, 161
	$CH{=}CH_2$	H	OCH_3	OCH_3	$KN(TMS)_2$, THF, 20°	(60)	133
C_{15}	OTBDMS	H	OCH_3	OCH_3	NaH, THF, 90 min	(80)	59
C_{17}	H	CH_3	$OCH_2C_6H_5$	H	NaH, THF, heat 1 h	(53)	55b

C_{11}



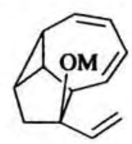
 I +  II 57

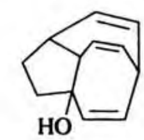
Reaction Conditions	Product(s) and Yield(s) (%)
KH, THF, 24 h	I (57)
KH, 18-crown-6, THF, 24 h	I (87) + II (13)

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.

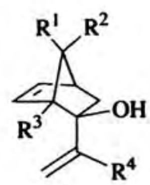
C_{12}

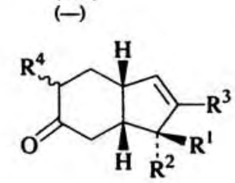




65

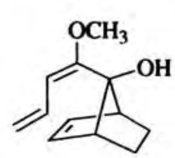
Reaction Conditions	Product(s) and Yield(s) (%)
M = Na, THF, 25°, 2 h	(100)
M = K, THF, 1°, few min	(—)



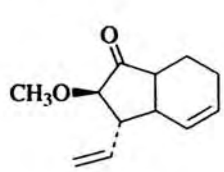


Carbon No.	R^1	R^2	R^3	R^4	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH_3	CH_3	CH_3	H	KH, THF, 20°	(85)	162
	CH_3	CH_2OH	H	CH_3	KH, THF	(94)	162
C_{13}	CH_3	CH_3	CH_3	CH_3	KH, THF	(85)	156

C_{12}



$KN(TMS)_2$ (excess), 18-crown-6, THF, 20°, 30 min



(50) 133

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

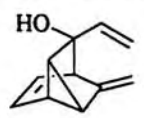
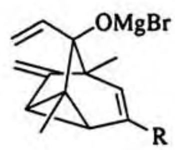
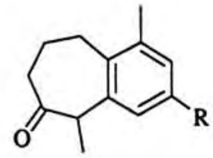
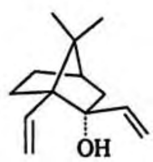
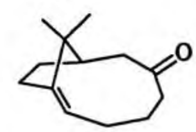
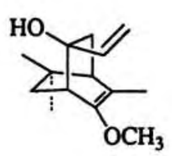
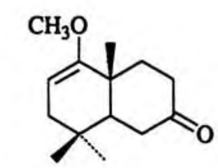
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		$KN(TMS)_2$, THF, heat 24 h	 (90)	63
		THF, reflux several h		64
C_{13}	R = H		(95)	
C_{14}	R = CH_3		(95)	
C_{13}		$KN(TMS)_2$, THF, 25°	 (86)	155
C_{14}		$KN(TMS)_2$, THF, 18-crown-6, 20°	 (66)	163

Table II. Cope Rearrangments of Bicyclic Vinylcarbinols (*Continued*)

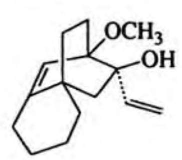
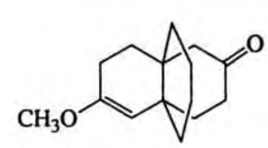
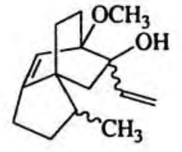
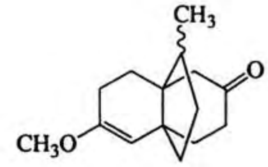
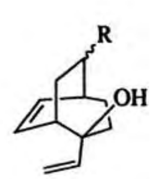
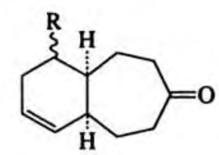
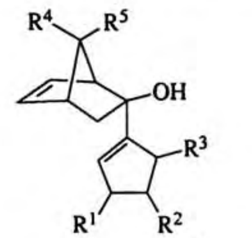
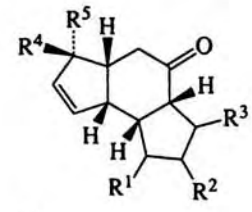
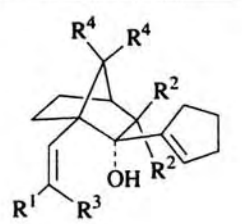
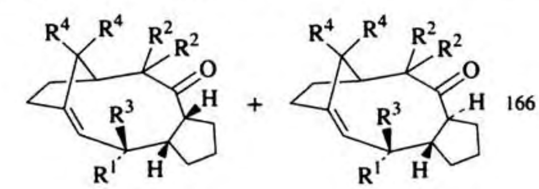
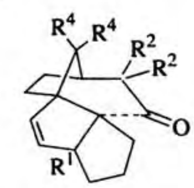
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		KH, THF, reflux 16 h	 (55)	62
		KH, THF, reflux 16 h	 (60)	62
		KH (1.2 eq), 18-crown-6, THF, reflux 1.5-2 h		23
	R = OC_4H_9-*n*		(70-75)	
	R = SC_4H_9-*n*		(59-61)	

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		$KN(C_3H_7\text{-}i)_2$ or KH, THF		

Carbon No.	R^1	R^2	R^3	R^4	R^5	Yield (%)	Refs.
C_{15}	H	$-CH_2-$		CH_3O	CH_3O	(40)	164
C_{16}	H	$-(CH_2)_2-$		CH_3O	CH_3O	(68)	164
C_{16}	$R^1, R^3 = -(CH_2)_2-$; $R^2 = H$			CH_3O	CH_3O	(76)	164, 165
C_{17}	H	$-(CH_2)_3-$		CH_3O	CH_3O	(85)	164
C_{22}	H	$-(CH_2)_3-$		CH_3S	$CH_2OTBDMS$	(84)	164
C_{22}	$R^1, R^3 = -(CH_2)_2-$; $R^2 = H$			CH_3S	$CH_2OTBDMS$	(76)	164
C_{23}	H	CH_3	C_2H_5	CH_3S	$CH_2OTBDMS$	(68-76)	164

Table II. Cope Rearrangments of Bicyclic Vinylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		$KN(TMS)_2$, THF, 25°	 I + II +  III	166

Carbon No.	R^1	R^2	R^3	R^4	I	II	III
C_{15}	H	CH_3	H	H	95	<5	(—)
C_{15}	OCH_3	H	H	H	40	40	0
C_{15}	H	H	OCH_3	H	32	11	17
C_{16}	CH_3	CH_3	H	H	83	(—)	(—)
C_{16}	H	CH_3	CH_3	H	62	10	(—)
C_{16}	OCH_3	CH_3	H	H	88	(—)	(—)
C_{16}	H	CH_3	OCH_3	H	0	(—)	51

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

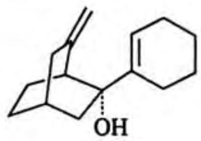
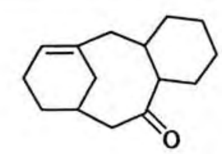
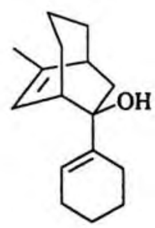
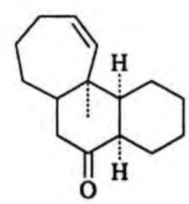
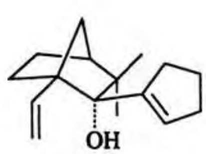
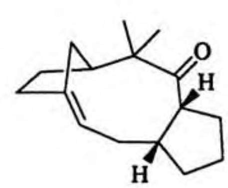
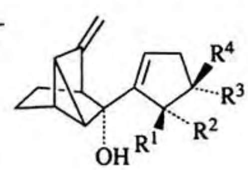
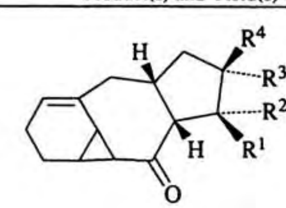
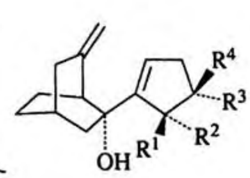
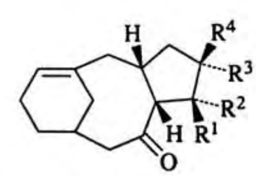
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		KH, THF, 25°, 10 h	 (70-85)	52
C_{16}		KH, DME	 (15-20)	53
		$KN(TMS)_2$, 18-crown-6, THF, 25°	 (91)[a]	167

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		$KN(TMS)_2$, THF		168
		$KN(TMS)_2$, THF		168

	R^1	R^2	R^3	R^4	
C_{16}	H	$-(CH_2)_2-$		H	(—)
C_{17}	i-(C_3H_7)	H	H	H	(0)
C_{17}	H	i-(C_3H_7)	H	H	(—)
C_{17}	C_2H_5	H	CH_3	H	(0)
C_{17}	H	C_2H_5	H	CH_3	(—)
C_{17}	H	$-(CH_2)_3-$		H	(—)

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

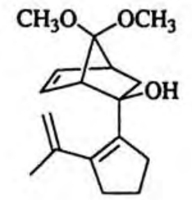
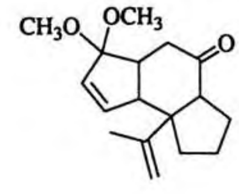
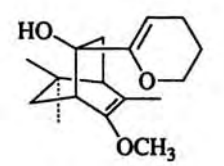
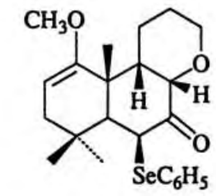
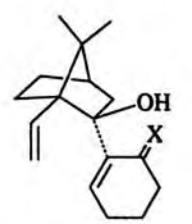
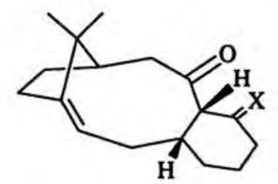
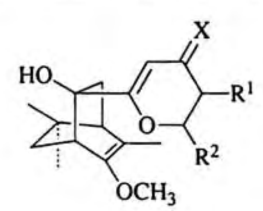
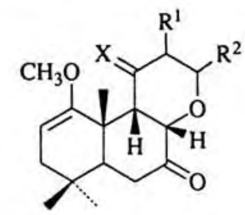
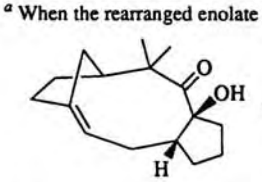
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		$KN(TMS)_2$, THF, 20°	 (—)	133
		1. KH, 18-crown-6, THF, 70°, 20 min 2. C_6H_5SeCl	 (79)	58
				
	X			
C_{17}	H	KH, THF, 25°	(—)	155
C_{19}	$-S(CH_2)_2S-$	KN(TMS), 18-crown-6, THF, 25°	(43)[b]	167
C_{19}	$-S(CH_2)_2S-$	KH, THF, 25°	(79)	155

Table II. Cope Rearrangements of Bicyclic Vinylcarbinols (*Continued*)

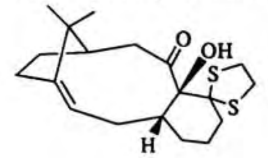
Carbon No.	Starting Material			Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				$KN(TMS)_2$, THF, 18-crown-6, 20°		163
	X	R^1	R^2			
C_{17}	H_2	H	H		(68)	
C_{19}	OCH_2OCH_3, H	H	H		(0)	
C_{22}	$-OCH_2C(CH_3)_2CH_2O-$	H	H		(0)	
C_{30}	OTBDMS, H	OTBDMS	CH_3		(0)	

[a] When the rearranged enolate was reacted with O_2 followed by triethyl phosphite



was formed in 87% yield.

[b] When the rearranged enolate was reacted with O_2 followed by triethyl phosphite



was formed in 44% yield.

Table III. Cope Rearrangements of Allylcycloalkanols

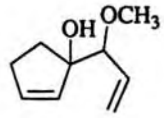
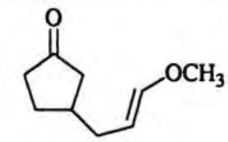
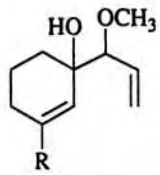
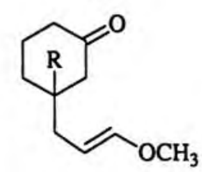
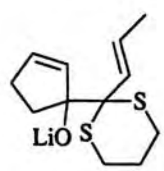
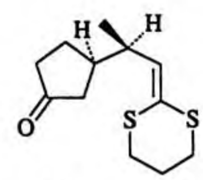
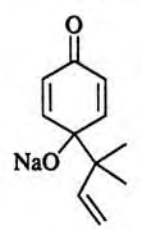
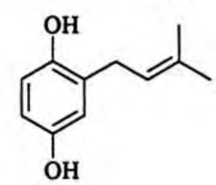
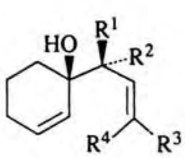
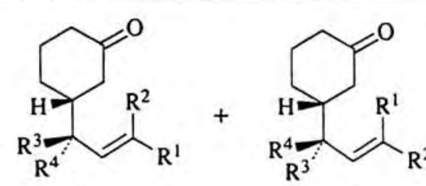
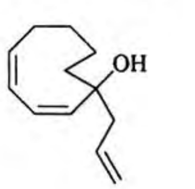
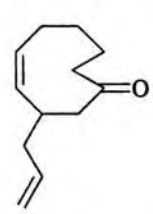
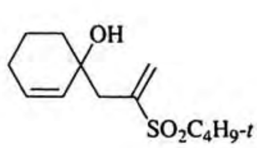
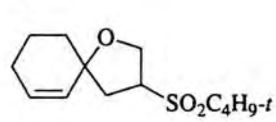
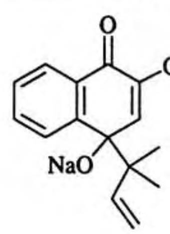
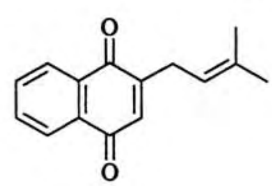
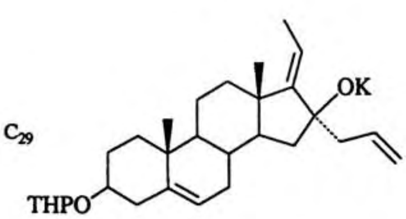
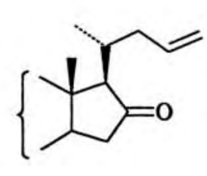
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		KH, DME, 85°, 9 h	 (64)	75b
		KH, DME, 85°, 30 h		75b
C_{10}	R = H		(70)	
C_{11}	R = CH_3		(10)	
C_{11}		THF, -78° to 25°, 2 h	 (89)	95
C_{11}		THF, H_2O, 25°, 3 h	 (70)[a]	169

Table III. Cope Rearrangements of Allylcycloalkanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		KH, DME, 85°, 30 h	 I + II	22
C_{12}		KH, THF	 (—)	94b
C_{13}		KH, THF	 (—)	96

R_1	R_2	R_3	R_4	I : II	
H	OCH_3	CH_3	H	4 : 96	(75-80)
OCH_3	H	CH_3	H	23 : 77	(75-80)
H	OCH_3	H	CH_3	0 : 98	(—)[b]
OCH_3	H	H	CH_3	30 : 70	(—)[b]

Table III. Cope Rearrangements of Allylcycloalkanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}		THF, H_2O, 25°, 3 h	 (95)[a]	169
C_{29}		Dioxane, reflux, 1 h	 (94)	66

[a] The starting material was prepared by treatment of the corresponding trimethylsilyl ether with sodium fluoride.

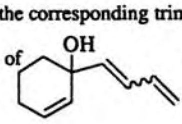
[b] In addition to the rearrangement product about 40% of  was obtained.

Table IV. Cope Rearrangements of 1,2-Divinylcyclobutanols

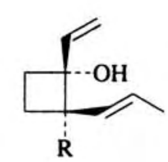
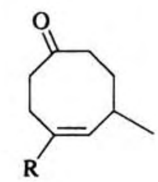
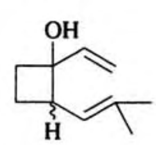
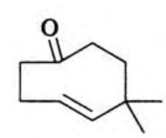
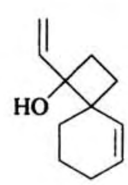
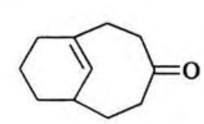
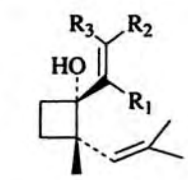
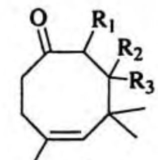
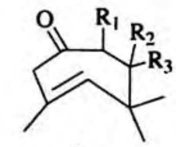
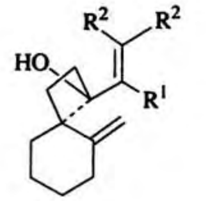
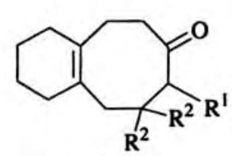
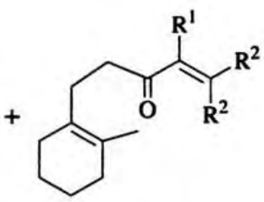
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, THF, 25°		170
C_9	R = H		(78)	
C_{10}	R = CH_3		(100)	
C_{10}		KH, THF	 (56)	171
C_{11}				
		KH, THF, 55°	(35)	69
		KH, THF	(—)	35
		KH, THF, rt	(80)	24

Table IV. Cope Rearrangments of 1,2-Divinylcyclobutanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, THF, 25°	 I +  II	24

Carbon No.	R^1	R^2	R^3	I : II	(%)
C_{11}	H	H	H	79:21	(62)
C_{12}	CH_3	H	H	5:95	(50)
C_{13}	H	CH_3	CH_3	67:33	(—)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
			 I +  II	24

Carbon No.	R^1	R^2	Reaction Conditions	Product(s) and Yield(s) (%)
C_{12}	H	H	THF[a]	I (34) + II (43)
C_{13}	CH_3	H	THF[a]	I (43) + II (43)
C_{13}	H	CH_3	KH, THF, 25°	II (—)

Table IV. Cope Rearrangements of 1,2-Divinylcyclobutanols (*Continued*)

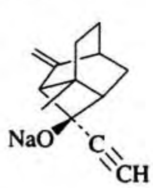
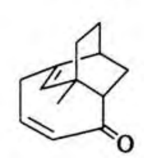
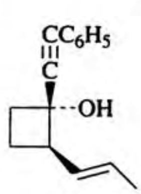
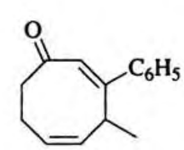
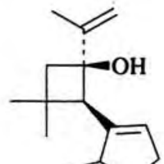
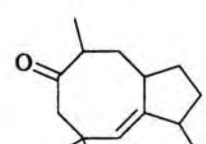
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		THF, -78° to 25°	 (62)	172
		THF, 65°	 (62)	172
C_{15}		KH, THF, 25°, 15 min	 (100)	170
		KH or $KN(C_3H_7\text{-}i)_2$	 (0)	170

Table IV. Cope Rearrangements of 1,2-Divinylcyclobutanols (*Continued*)

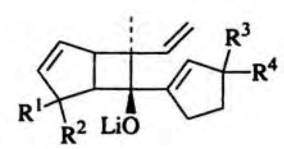
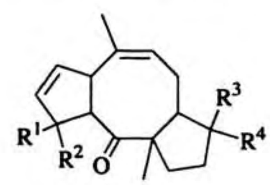
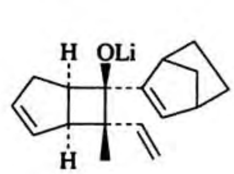
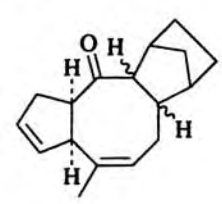
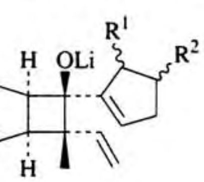
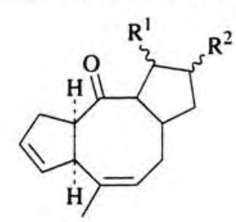
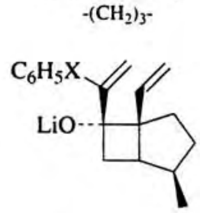
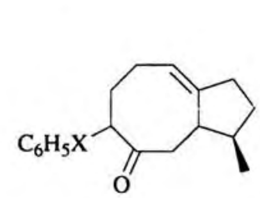
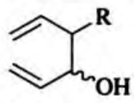
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		1. THF, -78° 2. CH_3I		
	R^1 / R^2 / R^3 / R^4			
C_{15}	H / H / H / H		(65)	70b
C_{17}	H / H / $-S(CH_2)_2S-$		(56)	70a
C_{18}	CH_3 / CH_3 / H / H		(65)	70a
C_{17}		THF, -78°	 (71)	173

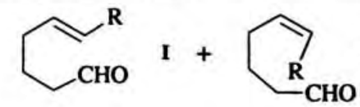
Table IV. Cope Rearrangements of 1,2-Divinylcyclobutanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, -78°		173
	R^1 / R^2			
C_{16}	$-CH_2-$		(94)	
C_{17}	$-(CH_2)_2-$		(80)	
C_{17}	C_2H_5 / H		(77)	
C_{18}	C_2H_5 / CH_3		(77)	
C_{18}	$-(CH_2)_3-$		(88)	
C_{18}	 X = S, Se	—	 (—)	70c

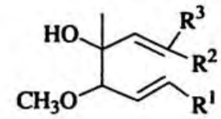
[a] The lithium salt was made in situ by addition of alkyllithium to the corresponding ketone.

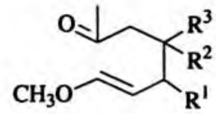
Table V. Cope Rearrangements in Open-Chain Systems





Carbon No.	Starting Material *threo* : *erythro*	R	Reaction Conditions	Product(s) and Yield(s) (%) I : II		Refs.
C_7	—	CH_3	KH, DME, 85°	—	(—)	71
C_7	79:21	CH_3	KH, DME, 85°, 6 h	71:29	(56)	73
C_7	79:21	CH_3	NMP, 204°, 10 h	67:33	(79)	73
C_7	12:88	CH_3	KH, DME, 85°, 4 h	72:28	(48)	73
C_7	12:88	CH_3	NMP, 204°, 11 h	79:21	(77)	73
C_8	—	C_2H_5	KH, DME, 85°	—	(—)	71





Ref. 75b

Carbon No.	R^1	R^2	R^3	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_8	H	H	H	KH, THF, 66°, 9.5 h	(85)	75b
C_9	H	H	CH_3	KH, DME, 85°, 6 h	(79)	
C_9	H	H	CH_3	KH, DME, 85°, 10.5 h	(81)	
C_{10}	H	CH_3	CH_3	KH, DME, 85°, 24 h	(11)	
C_{10}	CH_3	H	CH_3	KH, DME, 85°, 10.5 h	(81)	

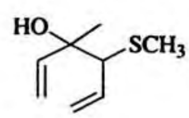
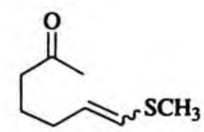
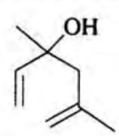
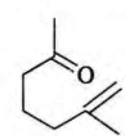
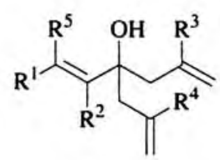
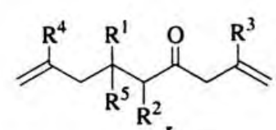
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		KH, THF, HMPA, 20°, 30 min	 (63)	21a

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

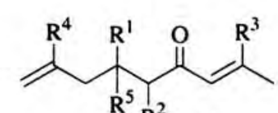
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_8		KH, 18-crown-6 (1.5 eq), THF, reflux	 (78)	174



KH, HMPA, 25°



I

\+ 

II

Ref. 76

Carbon No.	R^1	R^2	R^3	R^4	R^5	I : II	Yield (%)
C_9	H	H	H	H	H	5:1	(81)
C_{10}	CH_3	H	H	H	H	5:1	(83)
C_{10}	H	CH_3	H	H	H	3:1	(78)
C_{11}	CH_3	CH_3	H	H	H	3:1	(77)
C_{11}	H	H	CH_3	CH_3	H	4:1	(84)
C_{11}	CH_3	H	H	H	CH_3	—	(43)[a]
C_{12}	H	CH_3	CH_3	CH_3	H	3:1	(81)
C_{12}	CH_3	H	CH_3	CH_3	H	6:1	(86)
C_{13}	CH_3	H	CH_3	CH_3	CH_3	—	(46)[b]
C_{13}	CH_3	CH_3	CH_3	CH_3	H	5:1	(82)

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

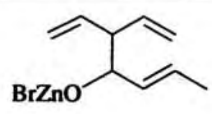
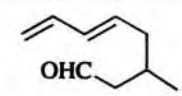
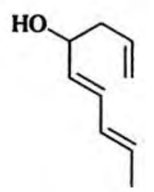
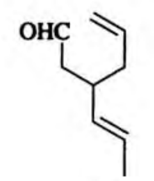
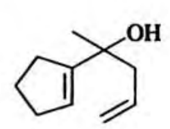
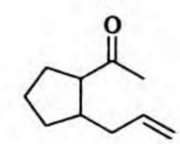
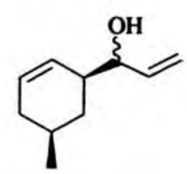
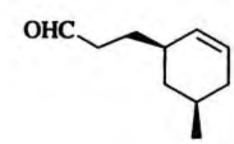
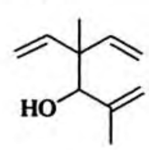
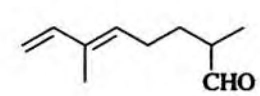
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		—	 (—)	106
		KH, 18-crown-6, THF, reflux several h	 (47)	121
C_{10}		KH, DME, reflux, 2.5 h	 (78)	175
		KH, 18-crown-6, DME, reflux	 (85)	176
		n-C_4H_9Li, THF	 (—)	105

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

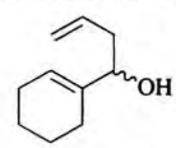
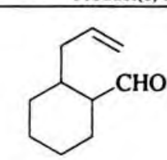
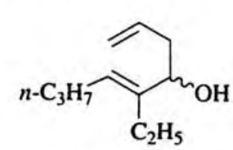
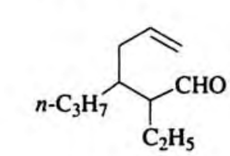
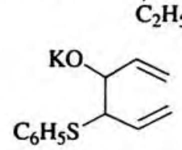
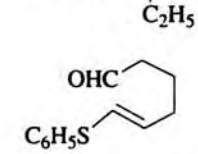
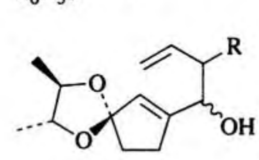
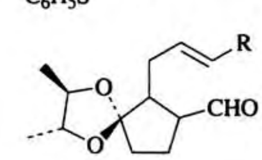
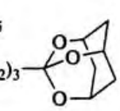
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, DME, reflux	 (69)	77
C_{11}		KH, DME, reflux	 (71)	77
C_{12}		THF, 25°, 1 h	 (42)	75b
				79
	R		ee	
C_{13}	H	KH, DME, 83°, 40 h	56 (—)	
C_{19}	C_6H_5	KH, DME, 0°, few min	0 (—)	
C_{23}	-$(CH_2)_3$- 	KH, DME, 83°, 40 h	56 (—)	

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

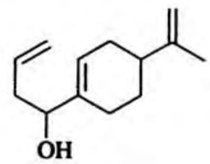
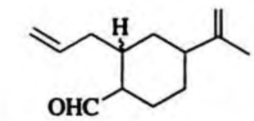
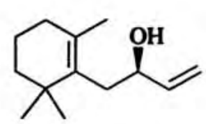
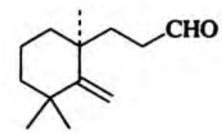
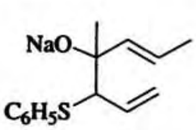
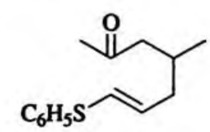
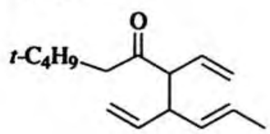
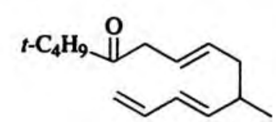
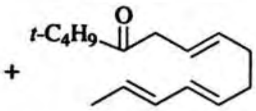
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_{13}		KH, DME		(73)	78
		KH, 18-crown-6, DME, reflux, 3 h		(—)	177
C_{14}		Ether, 25°, 6 h		(71)	10b
C_{15}		KH, THF, 17 h		(32)	82
			+ 	(39)	

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

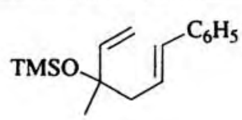
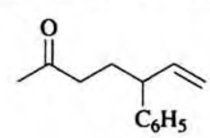
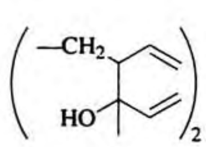
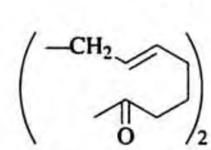
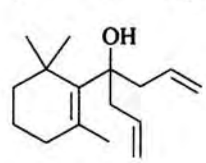
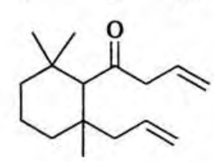
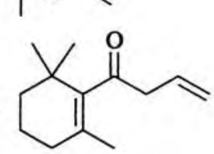
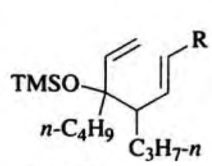
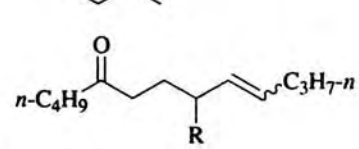
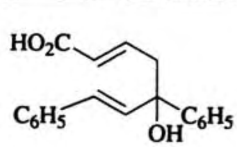
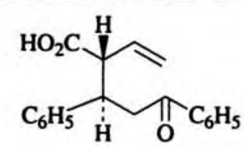
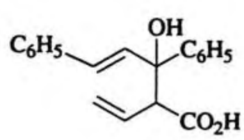
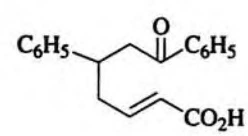
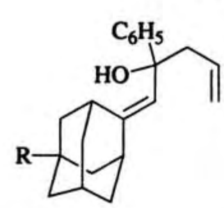
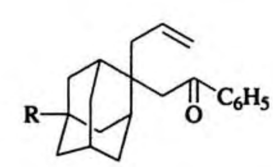
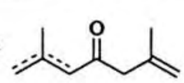
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_{16}		F^-, THF, 17 h		(0)	84
		KH, THF, reflux		(94)	85
C_{16}		KH, HMPA		(0)	76
			+ 	(70)	
		KH, 18-crown-6, THF, 65°, 1 h			48
C_{17}	R = CH_3		(78)		
C_{18}	R = C_2H_5		(75)		

Table V. Cope Rearrangements in Open-Chain Systems (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_{19}		Base (unspecified, 2 eq)		(87)	75a
		$LiN(C_2H_5)_2$, THF, -70° warm to 65°, 2 h		(—)	178
C_{21}		KH		(—)	179

[a] Cleavage product  was also formed in 35% yield as a mixture of double bond isomers.

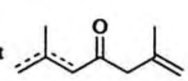
[b] Cleavage product  was also formed in 38% yield as a mixture of double bond isomers.

Table VI. Cope Rearrangements of 3-Methylene-1-vinylcycloalkanols

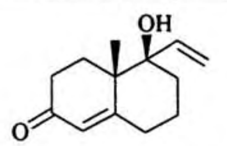
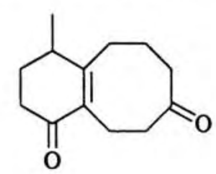
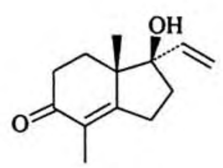
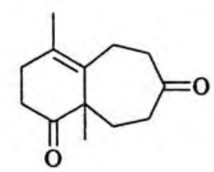
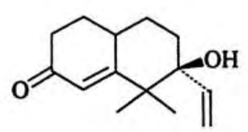
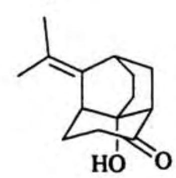
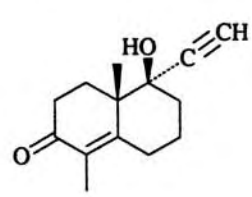
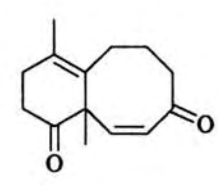
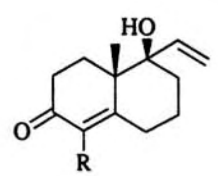
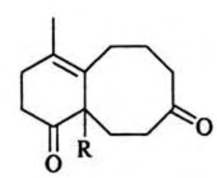
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		KOH, CH_3OH, H_2O	 (60)	86
		KOH, CH_3OH, H_2O	 (—)	87
C_{14}		KOH (4%), CH_3OH reflux 4 h	 (—)[a]	88
		KH, THF	 (65-70)	91

Table VI. Cope Rearrangements of 3-Methylene-1-vinylcycloalkanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KOH, CH_3OH, H_2O		
C_{14}	R = CH_3		(60)	87
C_{16}	R = $(CH_2)_2CO_2H$		(60)	90

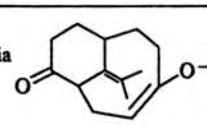
[a] The product was formed via 

Table VII. Cope Rearrangements that Contract Medium-Sized Rings

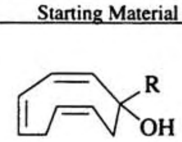
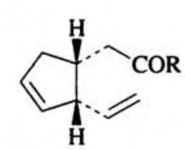
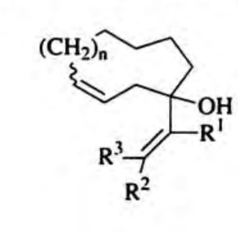
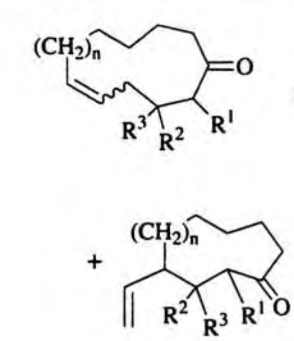
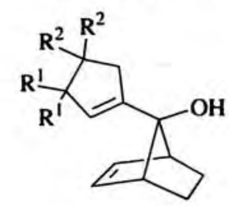
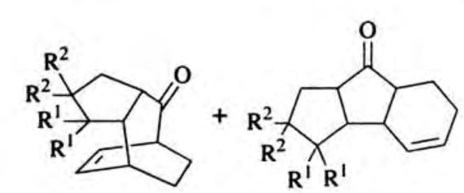
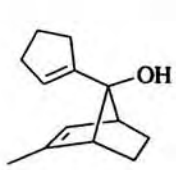
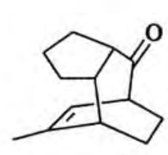
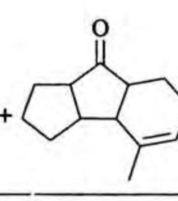
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				
C_9	R = H	KH, ether or THF, 25°	(—)	30, 94a
C_{10}	$R = CH_3$	NaH, THF, 66°, 3 h	(90)	93
C_{11}	$R = C_2H_5$	NaH, THF, 66°, 3 h	(90)	93

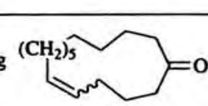
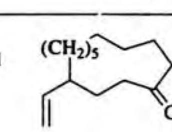
Table VIII. Substrates That Undergo Both [1,3] and [3,3] Rearrangements

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, HMPA	 I + II	

Carbon No.	n	R^1	R^2	R^3	Temp.	Time (h)	I	II	Refs.
C_{11}	1 *cis*	H	H	H	25°	2.8	(55)	(7)	122, 123
C_{12}	2 *trans*	H	H	H	25°	3.0	(59)	(8)	122, 123
C_{12}	2 *cis*	H	H	H	25°	27.5	(31)	(0)	122, 123
C_{15}	5 *trans*	H	H	H	60°	4.5	(57)	(9)	123
C_{16}	5	CH_3	H	H	54°	2.5	(51)	(11)	125
C_{16}	5	H	H	CH_3	100°	2.0	(33)	(8)	125
C_{16}	5	H	CH_3	H	102°	1.5	(18)	(1)	125
C_{18}	5	H	*i*-C_3H_7	H	100°	2.5	(19)	(4)	125
C_{18}	5	TMS	H	H	60°	4.0	(67)	(9)[a]	125
C_{18}	5	H	TMS	H	25°	11.0	(—)	(—)[b]	125

Table VIII. Substrates That Undergo Both [1,3] and [3,3] Rearrangements (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, 18-crown-6, THF	 I + II	28
	R^1 / R^2			
C_{12}	H / H		I (42) + II (14)	
C_{13}	CH_3 / H		I + II (—)	
C_{13}	H / CH_3		I + II (—)	
C_{13}		KH, 18-crown-6, THF	 (40) +  (15)	28

[a] The TMS group was lost during the rearrangement yielding  and 

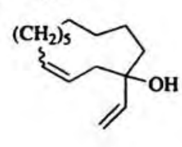
[b] No rearrangement took place but the TMS group was lost yielding 

Table IX. Cope Rearrangements That Involve Aromatic Bonds

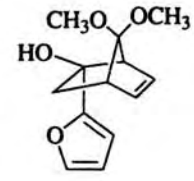
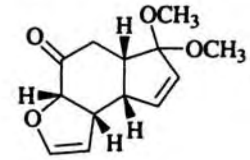
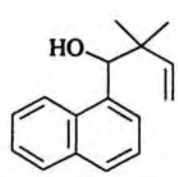
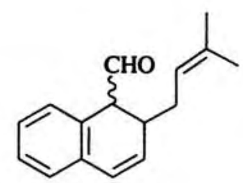
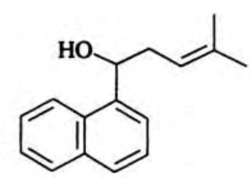
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		NaH, THF, 66°, 1 h	 (70)	54
C_{16}		KH, HMPA, 65°, 4 h	 (10)	97
			+  (57)	

Table IX. Cope Rearrangements That Involve Aromatic Bonds (*Continued*)

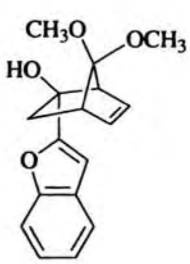
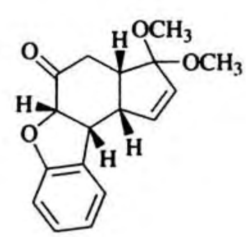
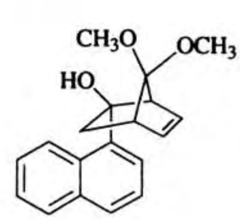
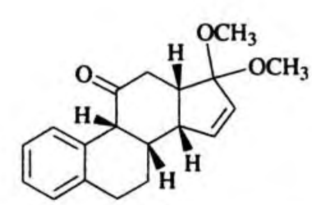
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		NaH, THF, 66°, 1 h	 (88)	56
C_{19}		NaH, THF, 66°, 1 h	 (75)	54

Table X. [5,5]-Sigmatropic Rearrangements

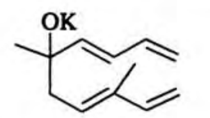
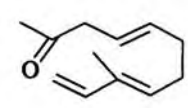
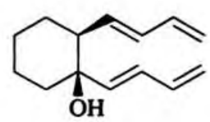
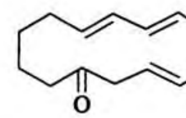
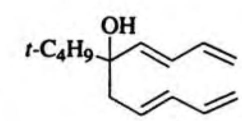
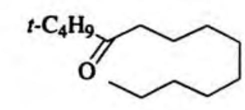
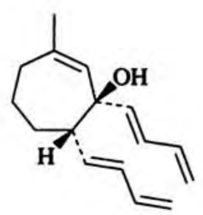
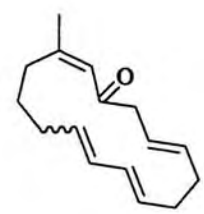
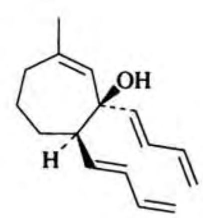
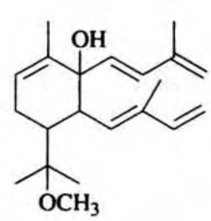
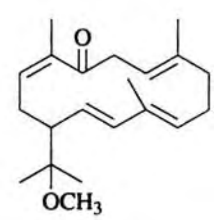
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}		THF, 1 h		(78)	102
C_{14}		KH, THF, 25°, 1 h		(90)	101, 102
C_{14}		1. KH, THF 2. H_2, Pd		(88)[a]	82
C_{16}		KH, THF, 25°, 25 min		(40)	40

Table X. [5,5]-Sigmatropic Rearrangements (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
		KH, THF, 25°, 25 min	" (61)		40
C_{21}		KH, 18-crown-6, THF, 2 h		(48-55)	180

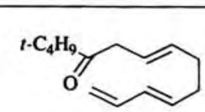
[a] The intermediate  was isolated but not purified.

Table XI. [1,3]-Sigmatropic Rearrangements of Allylcarbinols

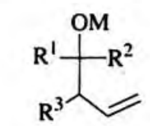
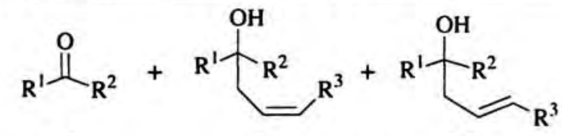
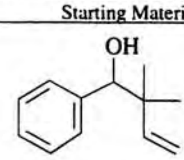
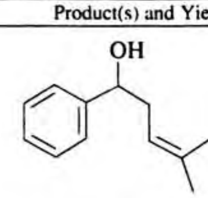
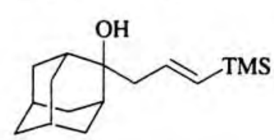
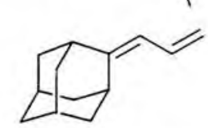
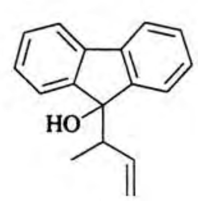
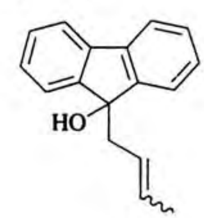
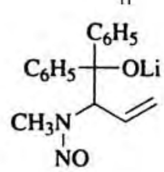
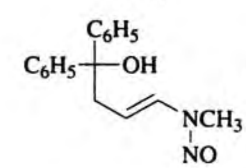
Carbon No.	Starting Material				Reaction Conditions			Product(s) and Yield(s) (%)		Refs.
					 I + II + III					
	M	R^1	R^2	R^3	Solvent	Temp	Time (h)	I : II : III		
C_9	Li	C_2H_5	C_2H_5	CH_3	Diglyme	162°	168	0 : 71 : 11	(7)	103
C_{11}	"	i-C_3H_7	i-C_3H_7	CH_3	DME	85°	96	0 : 72 : 28	(18)	103
C_{11}	"	C_2H_5	C_2H_5	i-C_3H_7	Diglyme	162°	48	0 : 73 : 27	(27)	103
C_{12}	MgBr	t-C_4H_9	i-C_3H_7	CH_3	THF	25°	96	13 : 60 : 27	(96)	18
C_{12}	Li	t-C_4H_9	i-C_3H_7	CH_3	THF	25°	12	0 : 81 : 19	(98)	103
C_{13}	MgBr	t-C_4H_9	t-C_4H_9	CH_3	THF	25°	6	<1 : 66 : 33	(91)	103
C_{13}	Li	t-C_4H_9	i-C_4H_9	CH_3	THF	25°[a]	1.2	<1 : 86 : 14	(91)	103
C_{13}	"	C_2H_5	C_6H_5	CH_3	Diglyme	162°	144	1 : 99 : 0	(77)	103
C_{13}	"	i-C_3H_7	i-C_3H_7	i-C_3H_7	THF	65°	48	0 : 50 : 50	(86)	103
C_{14}	"	i-C_3H_7	C_6H_5	CH_3	Diglyme	162°	72	75 : 9 : 6	(67)	103
C_{14}	"	i-C_3H_7	C_6H_{11}	CH_3	DME	85°	96	72 : 20 : 8	(82)	103
C_{14}	"	C_2H_5	C_2H_5	C_6H_5	THF	65°	6	0 : 100[b]	(76)	103
C_{15}	MgBr	t-C_4H_9	C_6H_{11}	CH_3	THF	25°	120	25 : 53 : 22	(84)	103
C_{15}	Li	t-C_4H_9	C_6H_{11}	CH_3	THF	25°	12	<1 : 81 : 19	(81)	103
C_{15}	"	t-C_4H_9	C_6H_5	CH_3	Diglyme	162°	48	6 : 76 : 18	(92)	103
C_{16}	MgBr	i-C_3H_7	i-C_3H_7	C_6H_5	THF	25°	12	<1 : 99[c]	(95)	103
C_{16}	Li	i-C_3H_7	i-C_3H_7	C_6H_5	THF	25°[a]	0.7	0 : 100[b]	(78)	103
C_{17}	"	C_6H_{11}	C_6H_{11}	CH_3	DME	85°	72	80 : 20[b]	(79)	103

Table XI. [1,3]-Sigmatropic Rearrangements of Allylcarbinols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}		KH, HMPA, 75°, overnight		(85)	97
C_{16}		KH, THF, 60°, 48 h		(88)[c]	181
C_{17}		CH_3Li, THF, 85°, 8 d Na, n-C_4H_9OH, reflux 2 h		(90)[d] (—)	104
		THF, KOC_4H_9-t		(30)	182

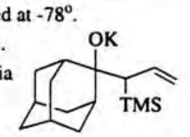
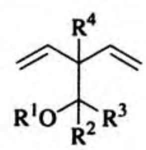
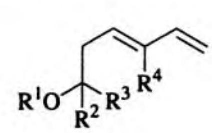
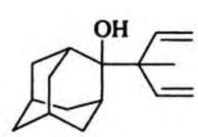
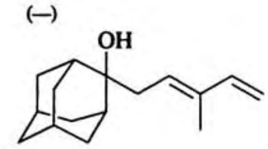
[a] The alkoxide was generated at -78°.
[b] The *cis:trans* ratio was 3:1.
[c] The product was formed via 
[d] The *cis:trans* ratio was 1:5.

Table XII. [1,3]-Sigmatropic Rearrangements of 3-Alkoxyalkyl-1,4-dienes





Carbon No.	Starting Material R^1	R^2	R^3	R^4	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9	ZnBr	CH=CHCH$_3$	H	H	THF	(19)[a]	106
C_{11}	H	CH=C(CH$_3$)$_2$	CH$_3$	H	n-C$_4$H$_9$Li, THF, reflux 2.5 h	(98)	107
C_{12}	ZnBr	n-C$_6$H$_{13}$	H	H	THF, 60°, 45 h	(7)[a,b]	106
					THF, DME, 60°, 240 h	(41)[b]	106
					Diglyme, 100°, 15 h	(100)	106
					HMPA, 100°	(100)	106
C_{13}	H	C$_6$H$_5$	H	CH$_3$	KH, THF, 0°	(—)	105
	H	n-C$_6$H$_{13}$	H	CH$_3$	KH, THF, 0°, 5 min	(—)	105
					n-C$_4$H$_9$Li, THF, 65°, 4 h	(—)	105
					NaH, HMPA, 0°, 30 min	(—)	105
					NaH, THF, 15-crown-5	(—)	105
C_{16}					n-C$_4$H$_9$Li, THF, 0°, 30 min	 (—)	105

[a] The ZnBr salt was formed in situ.

[b] The remainder was starting material.

Table XIII. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclopropanols

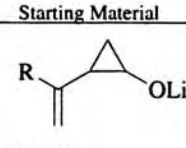
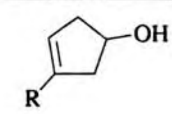
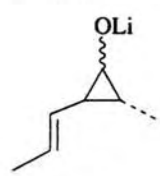
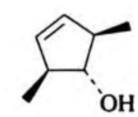
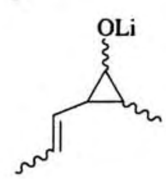
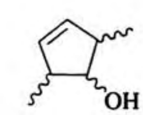
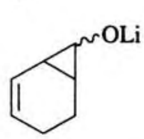
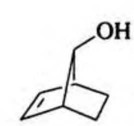
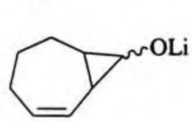
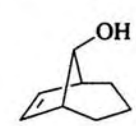
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Ether, 0° to 25°, 1 h		109
C_6	R = CH_3		(69)[a]	
C_9	R = t-C_4H_9		(90)	
C_{11}	R = C_6H_5		(95)	
C_7		Ether, 0° to 25°, 1 h	 (74)[a]	109
		Ether, 0° to 25°, 1 h	 (50-59)[a]	109
		Ether, 0° to 25°, 1 h	 (45)[a]	26
C_8		Ether, 0° to 25°, 1 h	 (48)[a]	109

Table XIII. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclopropanols (*Continued*)

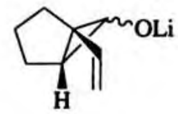
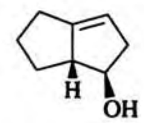
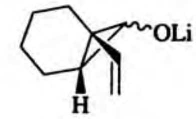
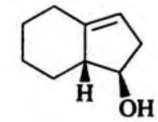
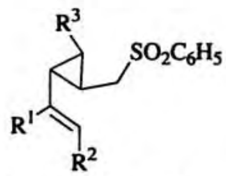
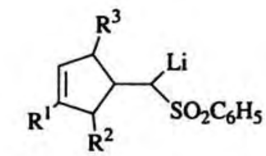
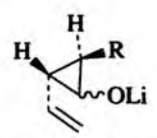
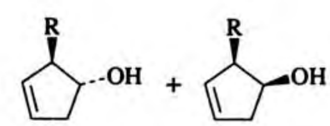
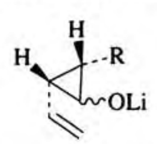
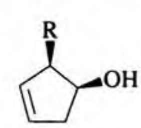
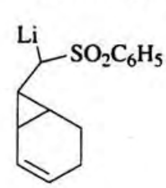
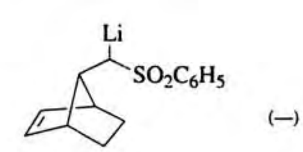
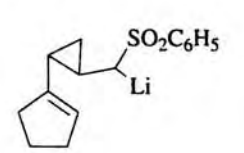
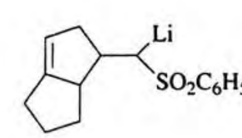
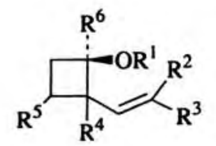
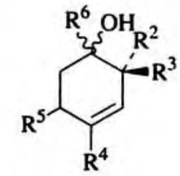
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Ether, 0° to 25°, 1 h	 (73)[a]	109
C_9		Ether, 0° to 25°, 1 h	 (61)[a]	109
		n-C_4H_9Li, THF, HMPA, -78° to -30°		83
	R^1 / R^2 / R^3			
C_{12}	H / H / H		(97)	
C_{13}	H / CH_3 / H		(—)	
C_{13}	CH_3 / H / H		(—)	
C_{14}	H / CH_3 / CH_3		(—)	
C_{20}	$(CH_2)_2C_6H_5$ / H / H		(—)	
C_{13}	 R = $(CH_2)_2C_6H_5$	THF, hexane, HMPA	 99:1 (77-82)[a]	26

Table XIII. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclopropanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}	 R = $(CH_2)_2C_6H_5$	THF, hexane, HMPA	 99:1 (78)[a]	26
C_{14}		THF, hexane, HMPA	 (—)	26
C_{15}		THF, hexane, HMPA	 (—)	26

[a] The lithium salt was formed in situ by n-C_4H_9Li cleavage of the β-chloroethyl ether of the corresponding alcohol.

Table XIV. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclobutanols

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				112

	R^1	R^2	R^3	R^4	R^5	R^6	Reaction Conditions	Yield (%)
C_7	Li	H	CH_3	H	H	H	THF, HMPA, 70°, 35 h	(65)[a]
C_7	$[KB(C_4H_9\text{-}s)_3]^+$	H	H	CH_3	H	H	HMPA, 70°	(0)[b]
C_7	H	H	H	CH_3	H	H	THF, HMPA	(72)[c]
C_9	CH_3	CH_3	CH_3	CH_3	H	H	C_2H_5OK, ether, THF	(63)
C_{10}	$[KB(C_4H_9\text{-}s)_3]^+$	H	H	C_6H_5	H	H	THF, HMPA, -78° to 25°, 2 h	(65-71)[d]
C_{11}	H	H	H	CH_3	$n\text{-}C_4H_9$	H	THF, HMPA, 70°, 4 h	(92)[c]
C_{11}	H	H	H	CH_3	H	$n\text{-}C_4H_9$	THF, HMPA, -78° to 25°, 2 h	(30)
C_{13}	H	H	H	C_6H_5	H	CH_3	THF, ether, -78° to 25°, 2 h	(42)[e]

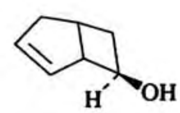
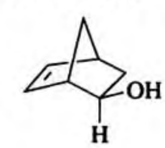
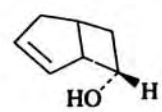
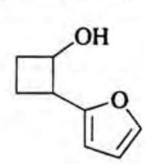
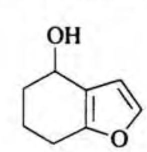
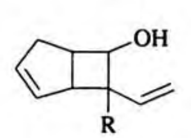
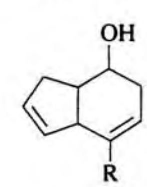
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_7		KH, THF, 25°, 3 h		(67)	183
		KH, THF, 65°	"	(—)	183

Table XIV. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclobutanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
C_8		KH, THF, heat		(33)	113
					112

	R	Reaction Conditions	Yield (%)
C_9	H	C_2H_5OK, ether, THF, 25°, 20 min	(65)
C_{10}	CH_3	C_2H_5OK, ether, THF, 25°, 15 min	(79)
C_{13}	$n\text{-}C_4H_9$	Li salt, THF, HMPA, 70°, 15 min	(89)[c]

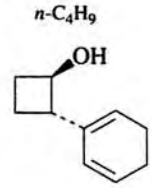
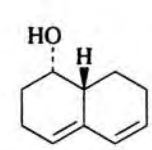
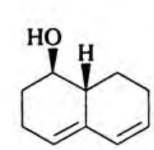
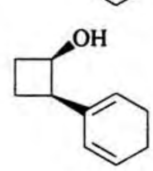
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		KH, THF, heat	 +  I (86) II (7)	113
		KH, THF, heat	I (67) + II (26)	113

Table XIV. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclobutanols (*Continued*)

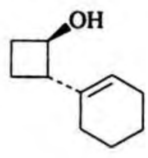
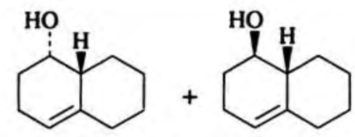
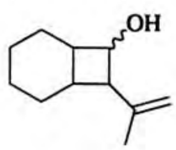
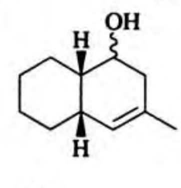
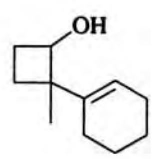
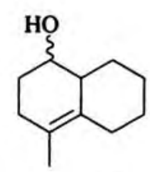
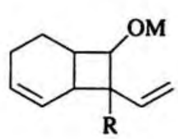
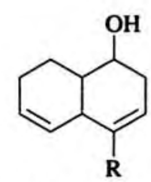
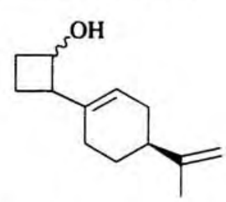
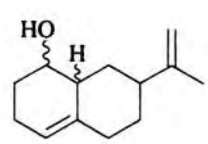
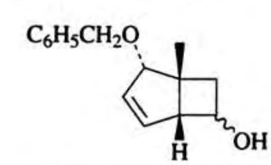
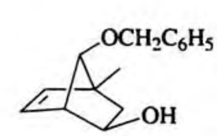
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, THF, 2 h KH, THF, 18-crown-6, 15 min	 70:30 (88) 10:90 (98)	184
C_{11}		KH, THF, reflux, 1 h	 (74)	113
		KH, THF, HMPA, 25°, 1 h	 (75)	112
				112
C_{11}	R = CH_3	M = Li, THF, HMPA, 70°, 9 h	(83)	
C_{14}	R = n-C_4H_9	M = K, THF, 25°, 15 min	(85)[f]	

Table XIV. [1,3]-Sigmatropic Rearrangements of 2-Vinylcyclobutanols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		KH, THF, heat, 1 h	 (87)	113
C_{15}		NaH, THF, heat	 (70)	55b

[a] The *cis:trans* ratio was 16:84.

[b] The borate complex resulting from reduction of the corresponding ketone with $KB(C_4H_9\text{-}s)_3H$ resists rearrangement.

[c] The lithium salt was prepared in situ by the reaction of the analogous borate complex with excess CH_3Li.

[d] The lithium salt was prepared by addition of n-C_4H_9Li to the corresponding ketone.

[e] The borate complex was prepared by reduction of the corresponding ketone with $KB(C_4H_9\text{-}s)_3H$.

[f] The potassium salt was formed with potassium ethoxide.

Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted 2-Alkenols

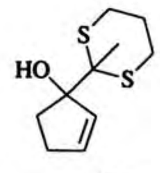
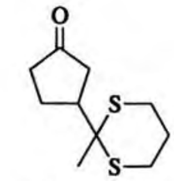
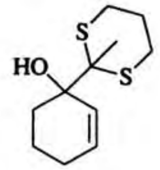
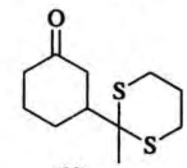
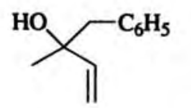
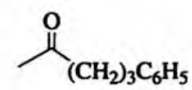
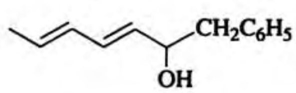
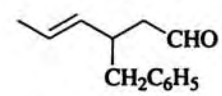
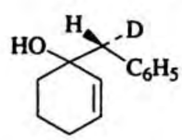
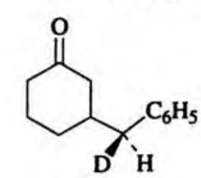
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		KH, HMPA, THF	 (53)	115
C_{11}				
		KH, HMPA, 25°, 24 h	(23)	115
		KH, TPPA[a], 25°, 45 min	(30)	120
C_{11}		KH, HMPA, 25°, 4 h	 (21)[b]	124
C_{13}		KH, HMPA, 100°	 (14)	121
C_{13}		KH, HMPA, 22°	 (—)	27

Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted 2-Alkenols (*Continued*)

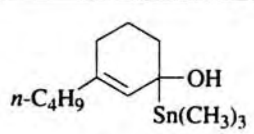
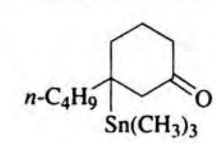
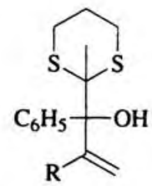
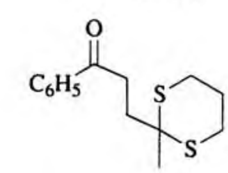
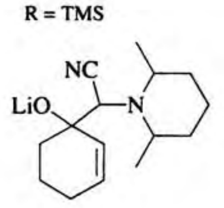
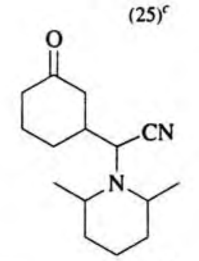
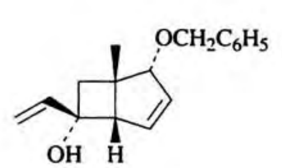
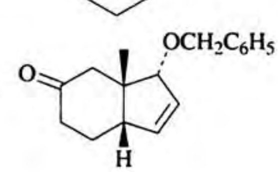
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, HMPA	 (—)	117
		KH, HMPA		
C_{14}	R = H		(27)	115
C_{17}	R = TMS		(25)[c]	120
C_{15}		THF, HMPA, 1.5 h[d]	 (50)	118
C_{17}		NaH, THF, heat, 1.75 h	 (10)	55b

Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted 2-Alkenols (*Continued*)

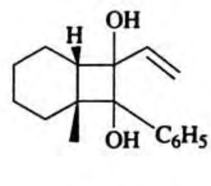
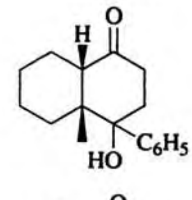
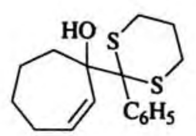
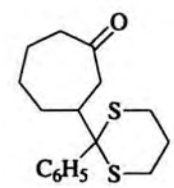
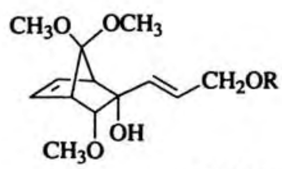
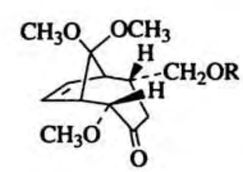
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH (excess), 18-crown-6, THF, reflux	 (0)	119
C_{17}		n-C_4H_9Li, THF, 24°, 1 h	 (84)	119
C_{19}	 R = TBDMS	KH, 18-crown-6, THF	 (56)	185

Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted 2-Alkenols (*Continued*)

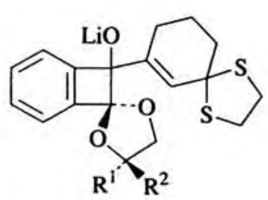
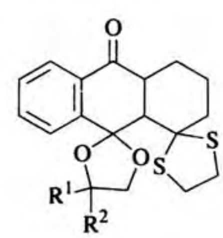
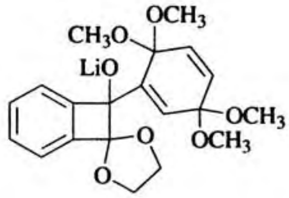
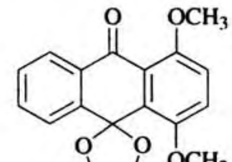
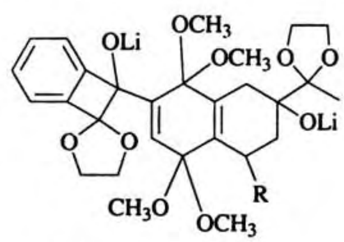
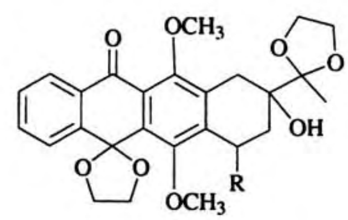
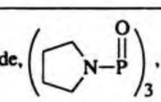
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		THF, 0° [e]		50
	R^1 R^2			
C_{18}	H H		(60)	
C_{19}	H CH_3		(—)	
C_{19}	CH_3 H		(—)	
C_{20}		THF, reflux[e]	 (70)	114

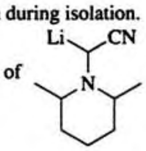
Table XV. [1,3]-Sigmatropic Rearrangements of 1-Substituted 2-Alkenols (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product (s) and Yield(s) (%)	Refs.
		THF, -30 to 66° [e]		114
C_{28}	R = H		(47)	
C_{29}	R = OCH_3		(63)	

[a] TPPA is tripyrrolidinophosphoramide,  , a solvent that is more polar than HMPA.

[b] In addition, toluene was isolated in 9% yield.

[c] The TMS group was replaced by hydrogen during isolation.

[d] The lithium salt was made by the addition of  to cyclohexene-3-one.

[e] The lithium salt was prepared by addition of the appropriate vinyllithium to a cyclobutanone.

Table XVI. [1,3]-Sigmatropic Rearrangements in Macrocyclic Systems

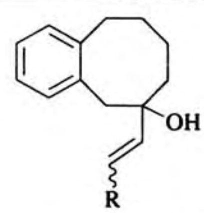
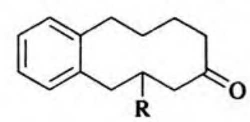
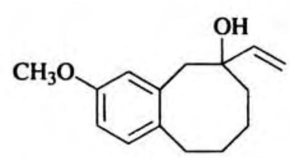
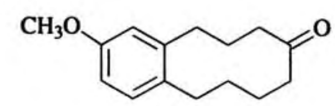
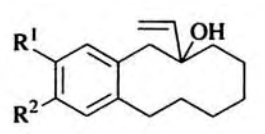
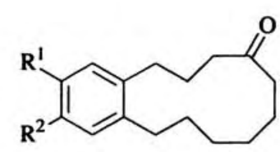
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, HMPA, 25°		123
C_{14}	R = H		(56)	
C_{16}	R = CH=CH$_2$		(20)	
C_{17}	R = CH=CHCH$_3$		(33)	
C_{15}		KH, HMPA	 (38)	124
		KH (8 eq), HMPA, 25°		186
	R^1 R^2			
C_{16}	H H		(70)	
C_{17}	H OCH_3		(94)	
C_{17}	OCH_3 H		(54)	

Table XVI. [1,3]-Sigmatropic Rearrangments in Macrocyclic Systems (*Continued*)

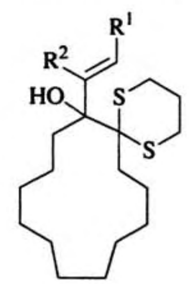
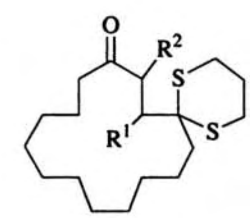
Carbon No.	Starting Material		Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
			—		115
	R^1	R^2			
C_{19}	CH_3	H		(21)	
C_{19}	H	CH_3		(28)	

Table XVII. [1,3]-Sigmatropic Rearrangements of Bridged Bicyclic Carbinols

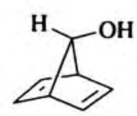
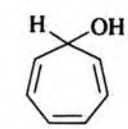
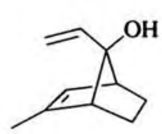
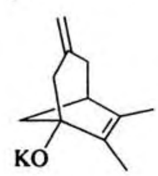
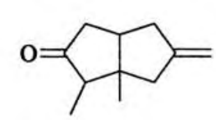
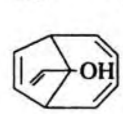
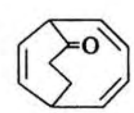
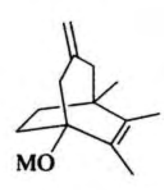
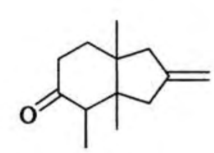
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		NaOH (0.08 M), CH_3OH, rt, 5 min	 (68)	126
C_{10}		KH, THF, 18 crown-6	 (36)	28
C_{11}		Thermolysis	 (0)	128
C_{11}		KH, THF, 24°, 2 min	 (100)	127
C_{12}		Thermolysis M = unspecified metal	 (0)	128

Table XVII. [1,3]-Sigmatropic Rearrangements of Bridged Bicyclic Carbinols (*Continued*)

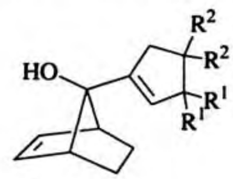
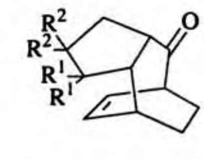
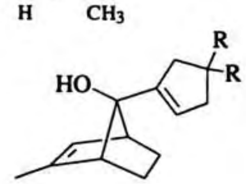
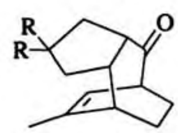
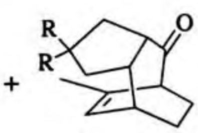
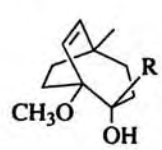
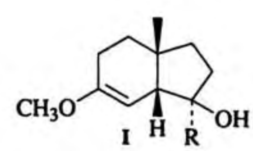
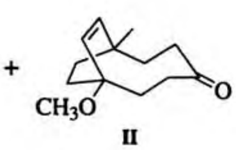
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, 18-crown-6, THF		28
	R^1 / R^2			
C_{12}	H / H		(20)	
C_{13}	CH_3 / H		(42)	
C_{13}	H / CH_3		(34)	
		KH, 18-crown-6, THF	 I +  II	28
C_{13}	R = H		I (24) + II (7)	
C_{14}	R = CH_3		I (21) + II (5)	
		KH, 18-crown-6, THF, reflux	 I +  II	129
C_{12}	R = CH_3		I (21)	
C_{13}	R = $CH{=}CH_2$		I (83) + II (13)	
C_{17}	R = C_6H_5		I (100)	

Table XVII. [1,3]-Sigmatropic Rearrangements of Bridged Bicyclic Carbinols (*Continued*)

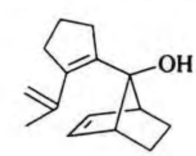
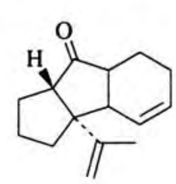
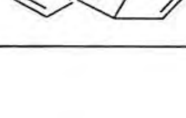
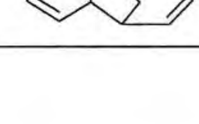
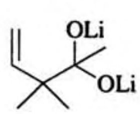
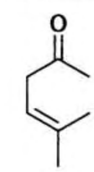
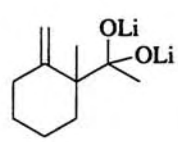
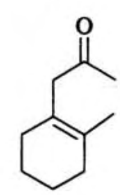
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		$KN(TMS)_2$, 18-crown-6, THF, 20°, 30 min	 (50)	133
		KH, THF, 24°, 2 min	 (100)	127

Table XVIII. [1,3]-Sigmatropic Rearrangements of 1,1,-Dialkoxy-Substituted Systems

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		THF, 65°, 4 h	 (80)[a]	130
C_{10}		Ether, 35°, overnight	 (—)	131

[a] There was no reaction with ether as the solvent.

Table XIX. [1,5]-Sigmatropic Shifts

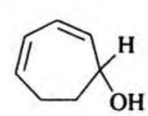
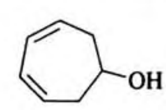
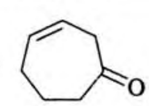
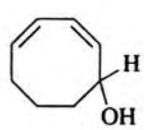
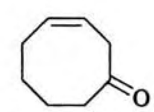
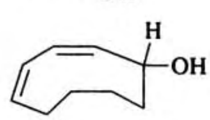
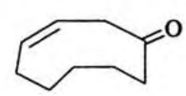
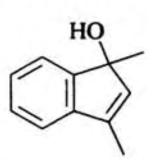
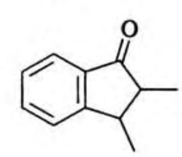
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			 I +  II	30, 121
		KH, THF	I (36) + II (54)	
		KH, 18-crown-6, THF	I (90)	
C_8		KH, THF	 (60)	30, 121
C_9		KH, THF	 (85)	30, 121
C_{11}		KH, HMPA, 135°, 2 h	 (0)[a]	132

Table XIX. [1,5]-Sigmatropic Shifts (*Continued*)

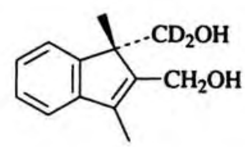
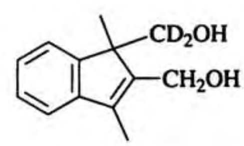
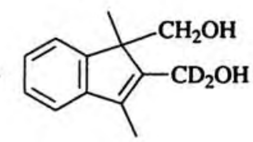
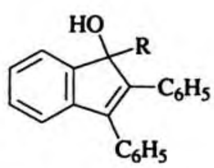
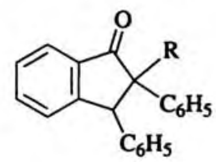
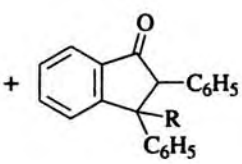
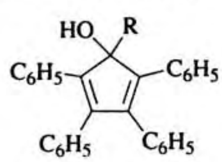
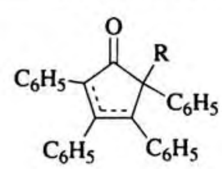
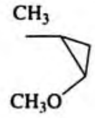
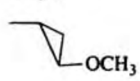
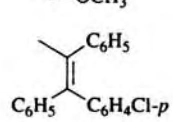
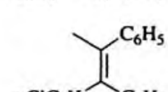
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		KH, THF	 (—)[b] +  (0)	132
C_{22}	 R = CH_3, 1-propenyl (*cis* or *trans*)	KH, HMPA, 80-95°, 2 h	 (—) +  (0)	132

Table XIX. [1,5]-Sigmatropic Shifts (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, HMPA, 30 min		132
	R			
C_{30}	CH_3		(76)	
C_{33}			(—)	
C_{33}			(—)	
C_{49}			(—)	
C_{49}			(—)	

[a] Only starting material was recovered.

[b] The starting material was optically active but the product was racemic.

Table XX. [2 + 2] Cycloreversion Reactions

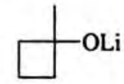
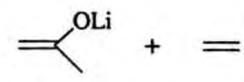
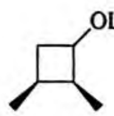
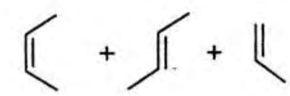
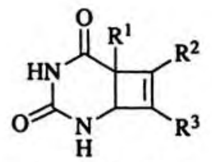
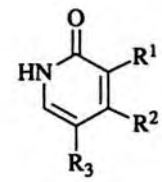
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_5		Glyme, 160-200°	 (—)	29
C_6		Glyme, 160-200°	 (—) 52:30:18	29
		KOC_4H_9-*t*, HOC_4H_9-*t*, reflux 4 h		137
	R^1 R^2 R^3			
C_7	H H CH_3		(60)	
C_7	F H CH_3		(50)	
C_8	H CH_3 CH_3		(65)	
C_9	H H *i*-C_3H_7		(84)	
C_9	CH_3 CH_3 CH_3		(83)	
C_{11}	H H *n*-C_5H_{11}		(83)	
C_{11}	F H *n*-C_5H_{11}		(70)	

Table XX. [2 + 2] Cycloreversions (*Continued*)

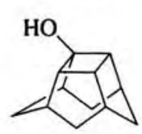
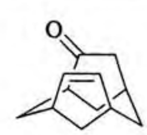
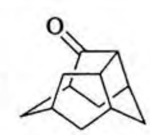
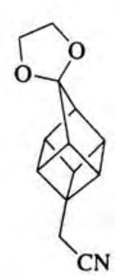
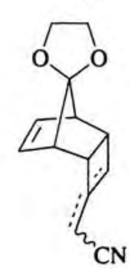
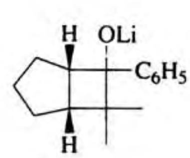
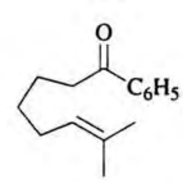
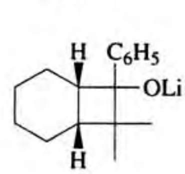
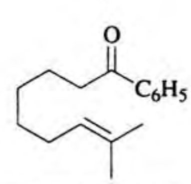
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		KOC_4H_9-*t*, HOC_4H_9-*t*, 170-200°	 (0) +  (90)	135
C_{13}		$LiN(C_3H_7$-$i)_2$, THF, 0°	 (100)	136
C_{15}		—	 (—)	29
C_{16}		Triglyme, 220°	 (—)	134

Table XXI. [2 + 4] Cycloreversions

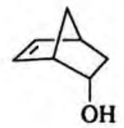
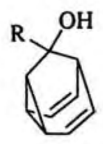
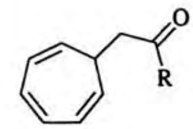
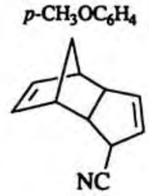
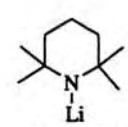
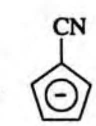
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_7		C_6H_5MgBr, ether, reflux 24 h	$C_6H_5CHOHCH_3$ (40-50)[a]	141
		NaH, ether, reflux	 (—) + CH_3CHO (—)	141
		KH, 18-crown-6, THF		144
	R			
C_9	H		(0)	
C_{10}	CH_3		(0)	
C_{11}	$CH{=}CH_2$		(60)	
C_{15}	p-BrC_6H_4		(86)	
C_{15}	p-ClC_6H_4		(98)	
C_{15}	C_6H_5		(90)	
C_{16}	p-$CH_3C_6H_4$		(91)	
C_{16}	p-$CH_3OC_6H_4$		(81)	
C_{11}		, hexane, THF, TMEDA, 25°	 +  (—)	187

Table XXI. [2 + 4] Cycloreversions (*Continued*)

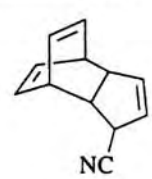
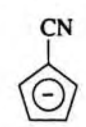
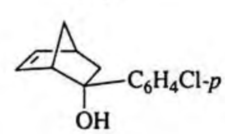
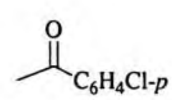
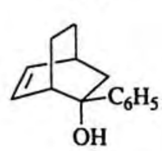
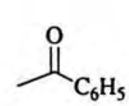
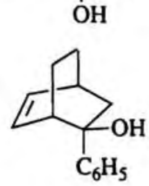
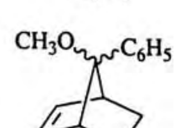
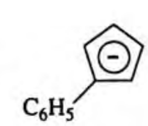
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		"	 +  (—)	187
C_{13}		KH, 18-crown-6, THF	 (—)	143
C_{14}		KH, HMPA, 90°, 1 h	 (45)	138
		KH, HMPA, 90°, 1 h	" (48)	138
		Na/K, DME, rt, 30 min	 (—) + $CH_2{=}CH_2$ (—)	188

Table XXI. [2 + 4] Cycloreversions (*Continued*)

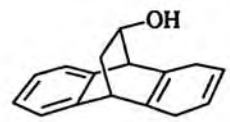
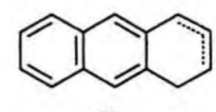
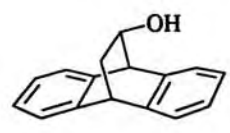
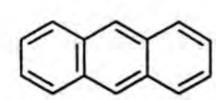
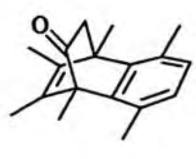
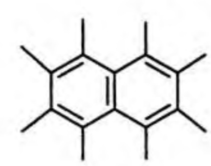
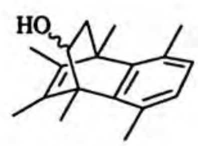
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16}				140
		KH, THF, rt, 18 h	(69)	
		NaH, dioxane, 101°, 3 h	(53)	
		KH, THF, rt, 66 h	 (60)	140
C_{18}		NaH, DMSO, 70°, 4.5 h	 (87)[b]	139
		NaH, DMSO, 70°, 4.5 h	" (95)	139

Table XXI. [2 + 4] Cycloreversions (*Continued*)

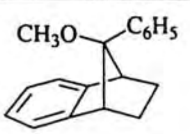
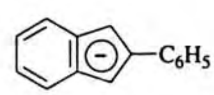
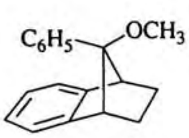
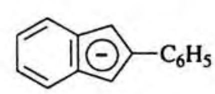
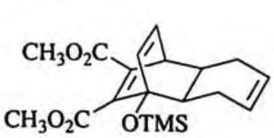
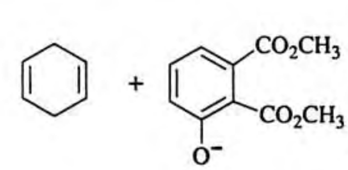
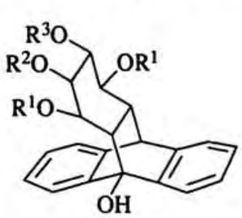
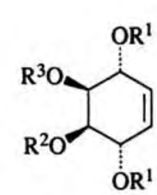
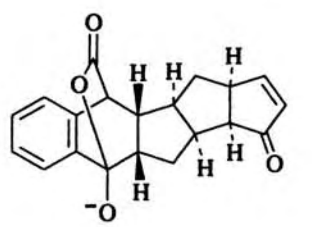
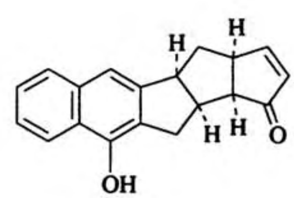
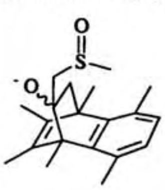
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Cs, K or Na, -40 to 0°, 2 h	 (—)	188
		Cs, K or Na, -40 to 0°, 2 h	 (—)	188
C_{19}		$(n\text{-}C_4H_9)_4N^+F^-$, THF, rt	 (—)	142
		KH, dioxane, 25°, 2 h		143
	R^1 / R^2 / R^3			
C_{24}	CH_3 / CH_3 / CH_3		(99)[c]	
C_{39}	$CH_2OCH_2C_6H_5$ / $-C(CH_3)_2-$		(99)[c]	

Table XXI. [2 + 4] Cycloreversions (*Continued*)

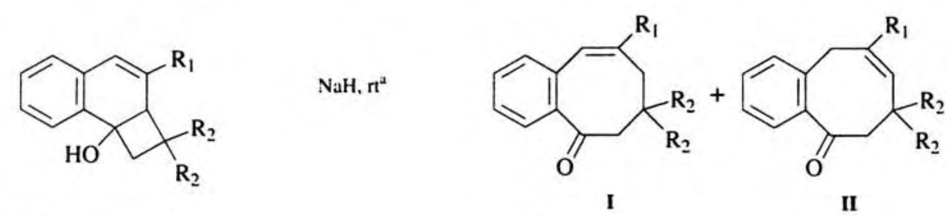
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20}		NaH, toluene, 150°, 12 h		190

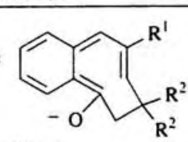
[a] The product was produced by addition of C_6H_5MgBr to the acetaldehyde formed by [2 + 4] cycloreversion.

[b] The reaction proceeded via 

[c] The other product was 9-anthrone, formed in unspecified yield.

Table XXII. Electrocyclic [4π + 2σ] Ring Opening Reactions

Carbon No.	Starting Material		Reaction Conditions	Product(s) and Yield(s) (%)		Refs.
			NaH, rt[a]	I + II		31
	R^1	R^2		I : II		
C_{14}	C_2H_5O	H	HMPA, 1.25 h	100:0	(75)	
C_{15}	CH_3	CH_3	HMPA, 6 h	100:0	(85)	
C_{16}	C_2H_5O	CH_3	HMPA, 3 h	100:0	(80)	
C_{16}	C_2H_5O	CH_3	DME, 3 h	35:65[b]	(90)	
C_{16}	C_2H_5S	CH_3	HMPA, 4 h	100:0[b]	(85)	
C_{17}	i-C_3H_7	CH_3	DME, 6 h	—	(0)[c]	
C_{20}	C_6H_5	CH_3	DME, 24 h	—	(—)[d]	
C_{20}	p-FC_6H_4	CH_3	DME, 4 h	100:0	(55)	
C_{20}	C_6H_5S	CH_3	DME, 3 h	83:17[b]	(85)	
C_{21}	p-$CH_3OC_6H_4O$	CH_3	DME, 3 h	100:0[b]	(80)	
C_{21}	p-$CH_3OC_6H_4S$	CH_3	DME, 5 h	85:15[b]	(75)	

[a] The reaction is presumed to occur via intermediate 

[b] The ratios of **I** and **II** depended on the workup conditions.

[c] The starting alcohol was recovered.

[d] Numerous unidentified products were formed.

Table XXIII. Electrocyclic [2π + 2σ] Ring Opening Reactions

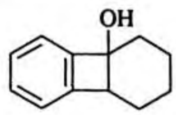
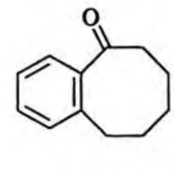
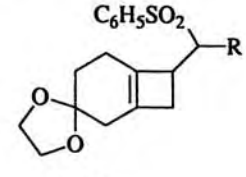
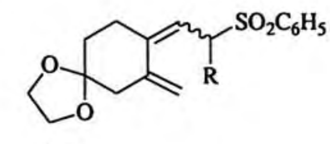
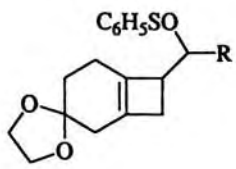
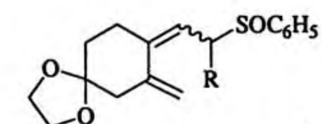
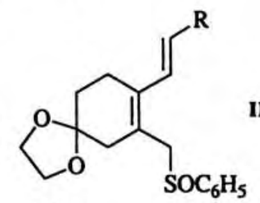
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}		KH, THF, 25°, 1 h	 (60)	146
		n-C_4H_9Li, ether, -30°, 10 min		32a
C_{17}	R = H		(92)	
C_{18}	R = CH_3		(23)	
		n-C_4H_9Li, ether, -30°, 10 min	 I +  II	32a
C_{17}	R = H		**I** (48) + **II** (48)	
C_{18}	R = CH_3		**II** (70)	

Table XXIII. Electrocyclic [2π + 2σ] Ring Opening Reactions (*Continued*)

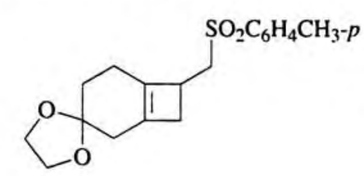
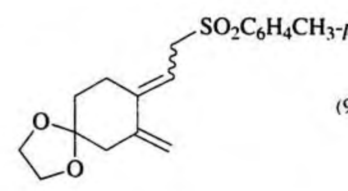
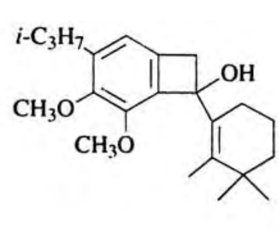
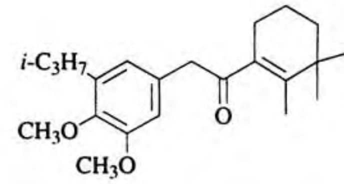
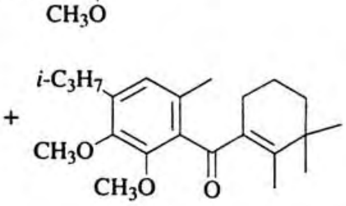
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}		n-C_4H_9Li, ether, -30°, 10 min	 (90)	32a
C_{22}		KOC_4H_9-t, HOC_4H_9-t	 (90) +  (5)	190

Table XXIV. Solvent-Induced [3,3]-Sigmatropic Rearrangements

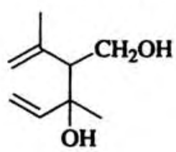
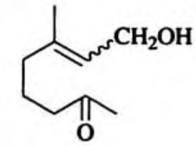
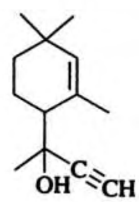
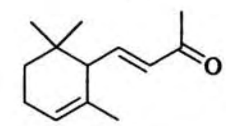
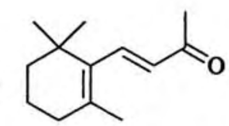
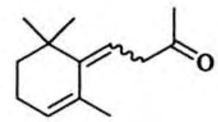
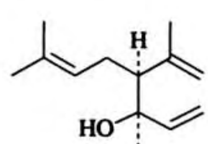
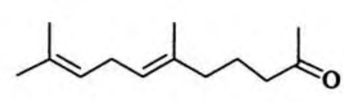
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		160-190°, NMP	 (60)	191
C_{13}		160°, 2 h	 I +  II +  III	99
			I : II : III	
		n-Decane	61 0 39 (84)	
		NMP	42 58 0 (90)	
		HMPA	36 64 0 (100)	
C_{13}		NMP (2 eq), 170°	 (—)	192

Table XXV. Fragmentation Reactions

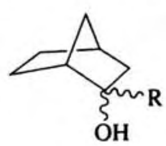
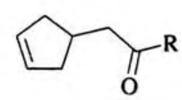
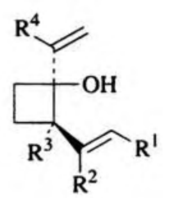
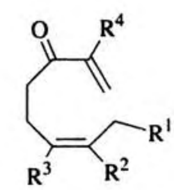
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		KH, HMPA, 30°		193
	R	time (h)		
C_8	CH_3	48	(45)	
C_9	C_2H_5	48	(50)	
C_{10}	n-C_3H_7	48	(48)	
C_{10}	i-C_3H_7	48	(21)	
C_{10}	$CH_2CH{=}CH_2$	24	(71)	
C_{11}	$CH_2C(CH_3){=}CH_2$	24	(76)	
C_{13}	C_6H_5	24	(8)	
C_{14}	$CH_2C_6H_5$	1	(85)	
		KH, THF, 25°		170
	R^1 R^2 R^3 R^4			
C_9	CH_3 H H H		(100)	
C_{10}	CH_3 H CH_3 H		(100)	

Table XXV. Fragmentation Reactions (*Continued*)

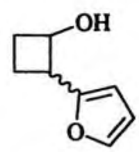
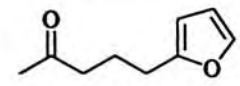
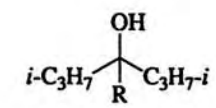
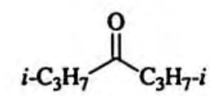
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		KH, THF, reflux	 (83)	113
		MNH_2, 242-392°, 3.5-6 h	 I + RH II	194
	R	M		
C_{10}	$n-C_3H_7$	Na	I (19) + II (58)	
	$i-C_3H_7$	Na	I (20) + II (24)	
C_{11}	$i-C_4H_9$	Na	I (37) + II (38)	
	$t-C_4H_9$	K	I (60) + II (—)[a]	
	$t-C_4H_9$	Na	I (52) + II (—)[a]	
	$t-C_4H_9$	Li	I (35) + II (—)[a]	
C_{12}	$CH_2C_4H_9-t$	Na	I (35) + II (36)	
	$CH_2C_4H_9-t$	K	I (64) + II (—)[a]	
C_{13}	C_6H_5	Na	I (72) + II (70)	

Table XXV. Fragmentation Reactions (*Continued*)

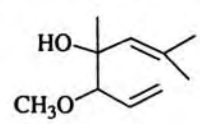
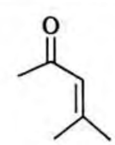
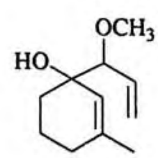
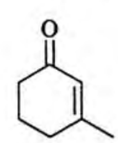
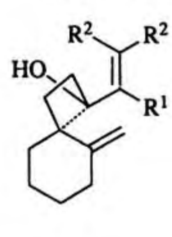
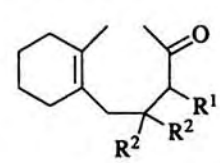
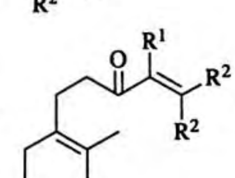
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}		KH, 85°, DME, 24 h	 (—)	75b
C_{11}		KH, 85°, 30 h	 (70)	75b
			 I +  II	24
	R^1 R^2			
C_{12}	H H	THF[b]	I (34) + II (43)	
C_{13}	CH_3 H	THF[b]	I (43) + II (43)	
C_{14}	H CH_3	KH, THF, 25°	II (—)	

Table XXV. Fragmentation Reactions (*Continued*)

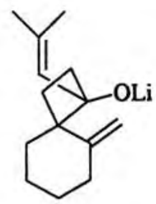
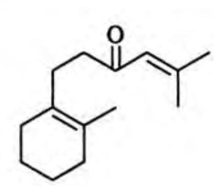
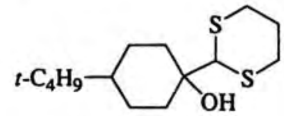
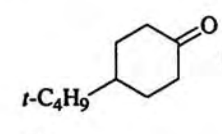
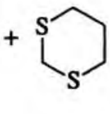
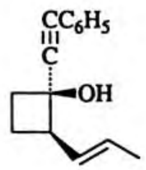
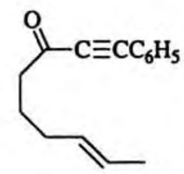
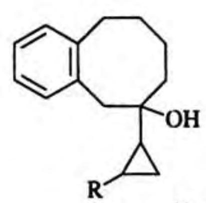
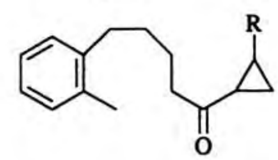
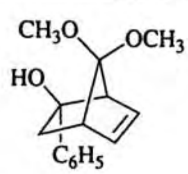
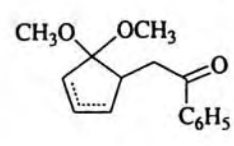
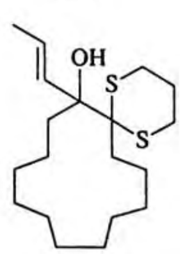
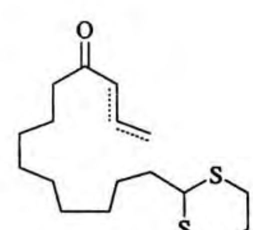
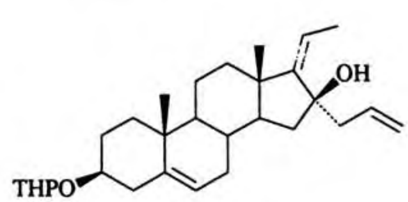
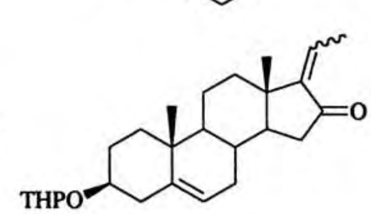
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}		THF^b	 (26)	24
C_{14}		KH, 18-crown-6, THF, 45°, 6 h	 (60) +  (10)	120
C_{15}		KH, C_6H_6, reflux 24 h	 (100)	170
C_{15}	 R = H, CH=CH_2	KH, HMPA	 (30)	123

Table XXV. Fragmentation Reactions (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}		KH, THF, 66°, 1.25 h	 (10)	54
C_{19}		KH, HMPA, THF	 (16)	120
C_{29}		KH, dioxane, reflux 1 h	 (—)	66

[a] A minor product was 2,2,4-trimethyl-3-pentanone.

[b] The lithium salt was made in situ from addition of an alkenyllithium to the corresponding ketone.

Table XXVI. *cis/trans* Isomerizations

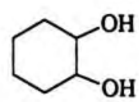
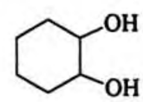
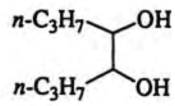
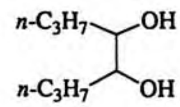
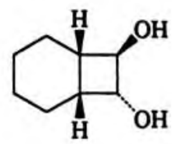
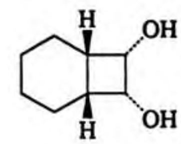
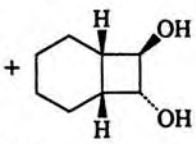
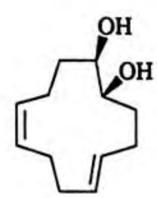
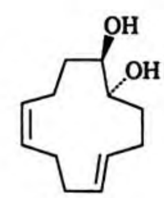
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_6		n-C_4H_9Li, diglyme, 155°, 3 h		195
	cis		*cis : trans* 3:97 (55)	
	trans		*cis : trans* 2:98 (65)	
C_8		n-C_4H_9Li, diglyme, 155°, 17 h		195
	meso		*meso : dl* 25:75 (57)	
	dl		*meso : dl* 25:75 (61)	
C_8		n-C_4H_9Li, diglyme, 155°, 17 h	 +  47:53 (58)	195
C_{12}		n-C_4H_9Li, diglyme, 155°, 17 h	 (—)	195

Table XXVI. *cis/trans* Isomerizations (*Continued*)

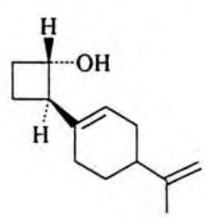
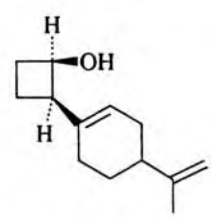
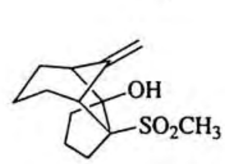
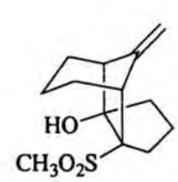
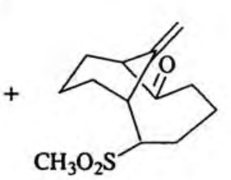
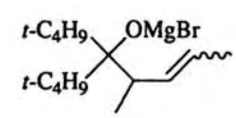
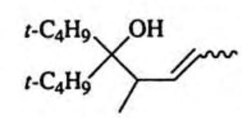
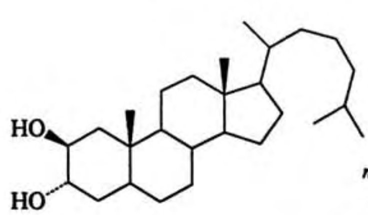
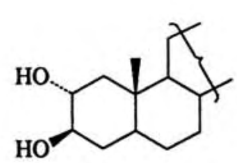
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}		KH, THF, 25°, 30 min	 (100)	113
			 +  I II	196
			I : II	
		KH, DME	4:1 (—)	
		KH, DME, 18-crown-6	1:1 (—)	
		KH, DME, [2.2.2]-cryptand	1:9 (—)	
		KOC_4H_9-*t* (0.2 eq), DMSO	0:95 (—)	

Table XXVI. *cis/trans* Isomerizations (*Continued*)

Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}	 *cis/trans* = 1:1	Ether, rt	 (100)[a] *cis/trans* = 1:3	197
C_{27}		n-C_4H_9Li, diglyme, 17 h, 155°	 (72)	195

[a] In the presence of excess CH_3MgBr, $(t\text{-}C_4H_9)_2COHCH_3$ was formed.

Table XXVII. Miscellaneous Reactions

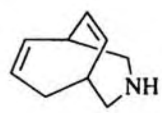
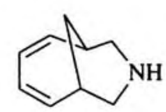
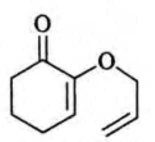
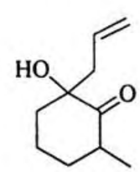
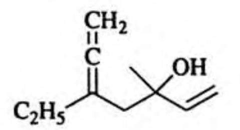
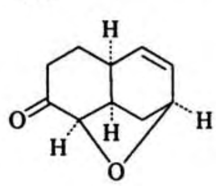
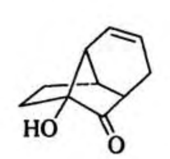
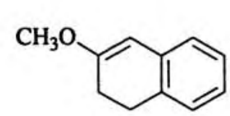
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_9		CH_3Li, ether, 30°, 1 min	 (90)	147
		$(CH_3)_2CuLi$, THF, -78°	 (—)[a]	149
C_{10}		KH, THF	Polymer (—)	198
		KOC_4H_9-*t* (10 eq), THF, 50°	 (94)	199
		1. KOC_4H_9-*t*, DMSO, 0-10°, 20 min 2, $(CH_3O)_2SO_2$	 (—)	200

Table XXVII. Miscellaneous Reactions (*Continued*)

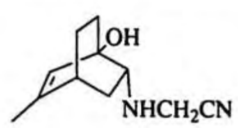
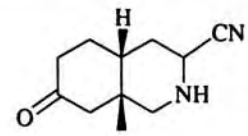
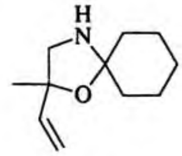
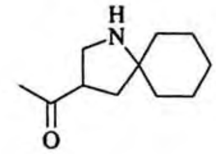
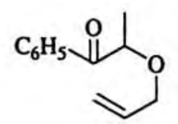
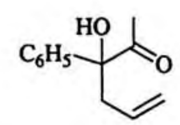
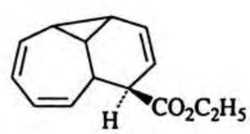
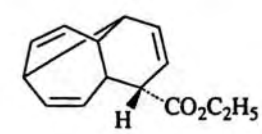
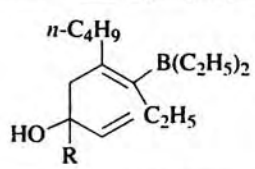
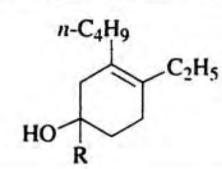
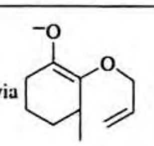
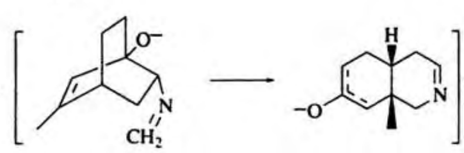
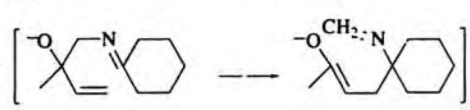
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}		KH (excess), THF, 23°	 (76-94)[b]	201
		KH, 18-crown-6	 (79)[c]	81
C_{12}		MH, toluene or THF, (M = Li, Na, or K)	 (—)[d]	149
C_{14}		LDA, THF, -70 to 0°, few min	 (—)	148

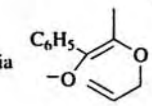
Table XXVII. Miscellaneous Reactions (*Continued*)

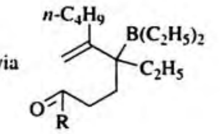
Carbon No.	Starting Material	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}		—	 (—)[e]	80

[a] The reaction proceeded via 

[b] The reaction proceeded via  ; KCN adds to the resulting imine to form the product.

[c] The reactions proceeded via intermediates 

[d] The reaction proceeded via 

[e] The reaction proceeded via 

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Carbonyl Methylenation and Alkylidenation Using Titanium-Based Reagents

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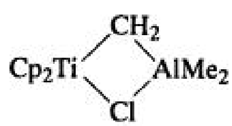
1. Introduction

Alkylidenation of the carbonyl group of ketones and aldehydes is among the most useful reactions of organic synthesis. The Wittig reaction of phosphoranes is probably the most widely used method of alkylidenation, (1-4) although a variety of other approaches have been developed to accomplish this transformation. (5-8)

The observation that titanium-based reagents can accomplish such a transformation (9-11) has provided a new approach to alkylidenation. Not only do these reagents accomplish alkylidenation of the carbonyl group of aldehydes and ketones, but they are also effective with esters, (10, 12-14) lactones, (10, 15, 16) amides, (12, 17) thioesters, (18) and certain other carboxylic acid derivatives. (19, 20) Alkylidenation of the carbonyl group of carboxylic acid derivatives cannot normally be accomplished by the Wittig reaction. (21, 22)

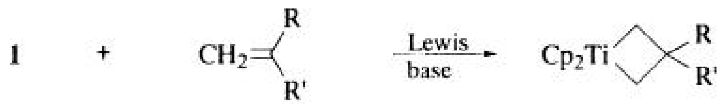
Initial interest in the reaction focused on methylenation using the titanium–aluminum complex known as the Tebbe reagent **1**. (9)



1

Pine, Grubbs, Evans, and co-workers explored the reactions of **1** with carboxylic esters and observed their conversion to enol ethers in high yield. (9, 10, 12)

Furthermore, **1** was also found to methylenate aldehydes and ketones, sometimes more effectively than the Wittig method. (23, 24) The related titanium metallacycles **2**, which are prepared from **1** and an alkene in the presence of a Lewis base, (25) accomplish similar alkylidenations. (15)



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During the same period Takai and co-workers reported a still undefined reagent **3** prepared from zinc, a dihalomethane, and titanium tetrachloride that was shown to methylenate aldehydes and ketones. (11) Modification of this mixture provides a reagent that accomplishes methylenation and alkylidenation of carboxylic acid derivatives. (14, 18, 19, 26) An alternative preparation of **3** by Lombardo (27, 28) has also received wide use.

$$Zn-CH_2X_2-TiCl_4$$

3

Reagents for carbonyl alkylidenation involving titanium–magnesium, (29) zirconium, (30, 31) tantalum, (32) tungsten, 33,33a molybdenum, (34-37) boron, (38) and chromium (39) have also been studied, but none has found such broad use in synthesis as **1** and **3**.

2. Mechanism and Stereochemistry

The structure of the Tebbe reagent (**1**) is well established as a titanium–aluminum metallacycle. It is the bridging methylene that is transferred to the carbonyl. (9) The reactive species is believed to be the titanium methylidene **4** generated when a Lewis base (LB) complexes with the aluminum atom of **1**. (9, 15, 40)

$$\mathbf{1} + \mathrm{LB} \longrightarrow \underset{\mathbf{4}}{[\mathrm{Cp_2Ti{=}CH_2}]} + (\mathrm{CH_3})_2\mathrm{ClAl}\cdots\mathrm{LB}$$

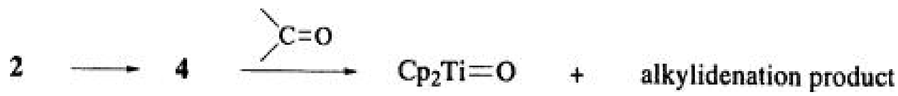
The titanium methylidene **4** and some homologs have also been generated thermally from the titanium metallacycles **2**. (15)

Intermediate **4** is very reactive and has never been isolated or observed spectroscopically. (41, 42) However, **4** has been observed as a tetrahydrofuran complex (43) and isolated as its phosphine complex (40, 44-46) Homologous phosphine complexes are known, (47) although their use in alkylidenation has not been reported. Intermediate **4** is generally classified as a nucleophilic carbene in an operational description of its reactivity. (32, 48)

In contrast to **1** and **2**, there appears to be little information about the species involved in the reagent mixture **3**. It is generally considered to be a *gem*-dimetallamethane. (11, 49-53) Here, functional group specificity seems to depend on reaction conditions, (18, 19) and even on the mode of preparation of the reagent. (27, 28)

In the absence of an added Lewis base, reaction of **1** with an ester such as methyl benzoate proceeds slowly ($t_{1/2}$ » 1 hour) to produce the enol ether. The reaction is first order in reagent and first order in ester. The large negative entropy value for this reaction suggests that a complex intermediate forms which then leads to product. (54) When a Lewis base is added to the reaction mixture, methylenation is quite rapid and is usually complete in minutes. In this case the Lewis base presumably complexes with the aluminum portion of **1** to free **4** for reaction with the carbonyl group. Ketones and amides react rapidly even in the absence of added Lewis base.

The metallacycles **2** react by a thermal process in which an alkene is eliminated to provide **4**. (40, 55) It has been suggested that a driving force for alkylidenation of a carbonyl by **2** is the formation of titanocene oxide. (56)



Alkylidenation of a carbonyl group can give either *E* or *Z* stereoisomers. Within a limited number of experimental examples, the *Z* isomer generally predominates. This result has been observed for esters, (14, 50) ketones, (14) thioesters, (18) and silyl esters. (19) By contrast, amides lead predominately to *E* enamines. (18) In all of these classes of compounds the degree of stereoselectivity is variable and appears to be related to the size of the groups surrounding the carbonyl. (18)

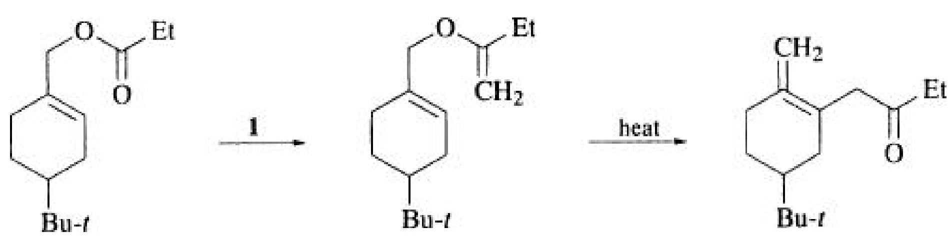
3. Scope and Limitations

These titanium-based reagents were initially explored to supplement the Wittig alkylidenation. The Wittig reaction has some synthetic limitations. Wittig reagents do not alkylidenate the carbonyl group of esters and other carboxylic acid derivatives; the reaction rate is low because of steric hindrance at the carbonyl, and there is a tendency for enolization to occur with certain substrates.

3.1. Methylenation of Esters

Reagent **1** converts esters to enol esters in high yield. (9, 10, 12) Metallacycles **2**, though not widely used, also acomplish the same transformation. (15) Reagent **1** provides the only one-step synthesis of a vinyl ether from an ester. It reacts with a large variety of substrates including aromatic, aliphatic, and cyclic esters (lactones) as well as formates, carbonates, silyl esters, and thioesters.

In addition to the isolation and use of enol ethers as synthetic products, one useful application associated with **1** is the ability to convert esters with an appropriately positioned double bond to products derived from a subsequent electrocyclic rearrangement. (13, 57-63) In some reactions Claisen rearrangement occurs without isolation of the enol ether intermediate. (57, 61, 63) It has been suggested that the aluminum- or titanium-containing byproducts function as Lewis acid catalysts for the rearrangement.



The Zn - CH_2X_2 - $TiCl_4$ mixture **3** has had very limited use for ester methylenation. (13, 57, 64)

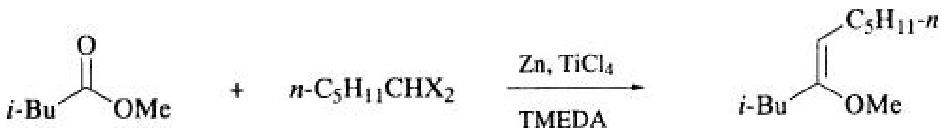
3.2. Alkylidenation of Esters

Reagents **1** and **2** only accomplish methylenation of the ester carbonyl group. However, the use of 1,1-dihaloalkanes instead of dihalomethanes in the preparation of **3** leads to a new reagent **5** that accomplishes general alkylidenation of esters. (14) Tetramethylethylenediamine (TMEDA) is required, and the reagents are mixed in a different order than that used for **3**.

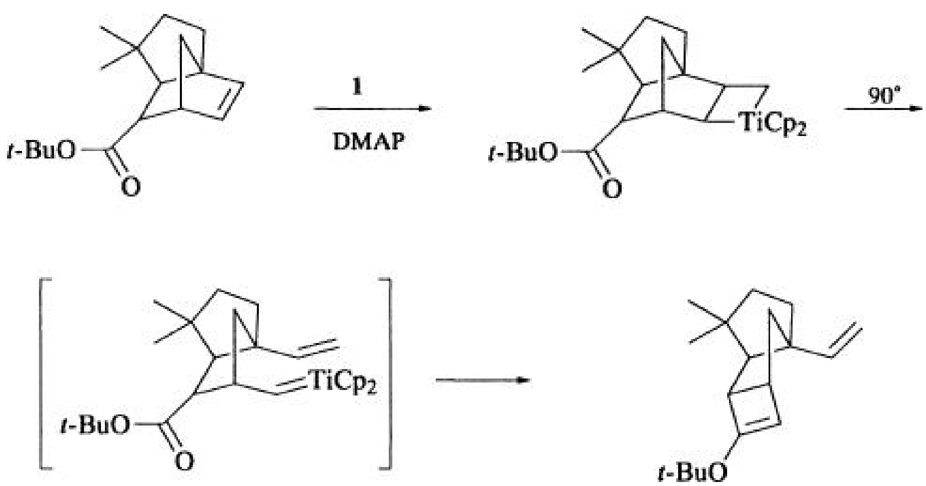
$$Zn-RCHX_2-TiCl_4-TMEDA$$

5

One may speculate that TMEDA complexes with the metal of the mixture to enhance reactivity toward an ester carbonyl group. The process produces mixtures of geometrical isomers in which the *Z* stereoisomer predominates. (14, 50) The difficulty in forming the requisite dihaloalkanes can be the limiting step in such an application.

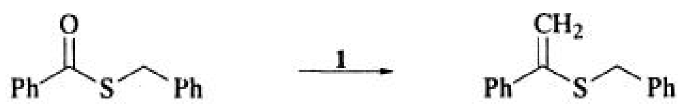


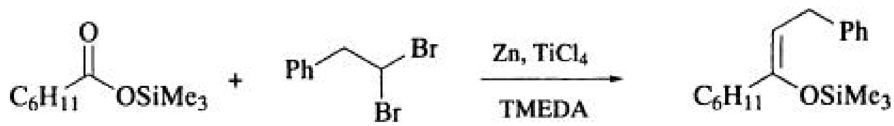
An intramolecular ester alkylidenation was used in a synthesis of capnellene. (65, 66) A titanium metallacycle **2** was formed from a norbornene derivative containing an ester by using **1** in the presence of *p*-dimethylaminopyridine (DMAP). The strained alkene of norbornene formed a particularly stable metallacycle, (66) while the hindered *endo*-*tert*-butyl ester did not react with **1**. Subsequent heating of the metallacycle derivative generated the titanium alkylidene which then accomplished an intramolecular alkylidenation of the ester.



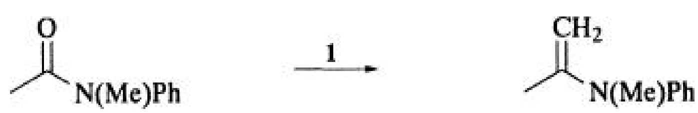
3.3. Reactions with Other Carboxylic Acid Derivatives

Silyl esters and thioesters react with **1** (67) and **5** (18, 19) to produce the corresponding enol ethers by a process similar to that discussed above for esters.

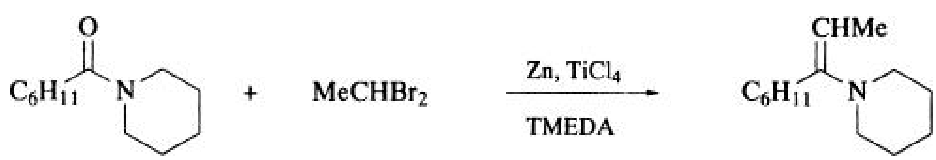




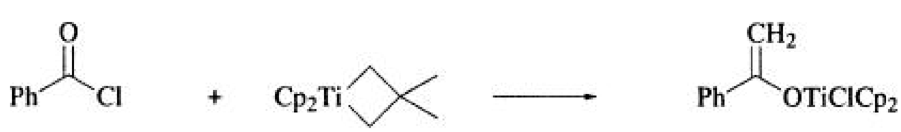
Amides react with **1** to give methylenenamines. (12)



The method provides an attractive alternative to established methods of enamine formation. (68-70) Difficulty in recovery of unstable enamines is often a limitation of the procedure. However, alkylation of the enamine formed with **1** can, in principle, provide the product of amide alkylidenation. There is one report of an amide alkylidenation using **5**. (18)



Acyl halides react with **1** or **2** to give titanium enolates rather than the chloro-vinyl products expected from carbonyl methylenation. (71-73) The alternative sequence has been attributed to the lability of the halide in an initially formed titanium oxametallacycle. This route to titanium enolates and their subsequent alkylation does have synthetic utility. (73)



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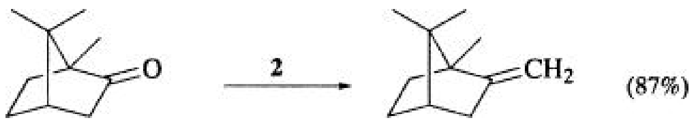
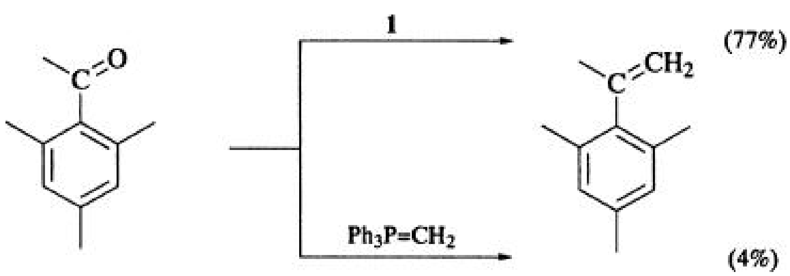
Anhydrides and imides follow pathways similar to that of an acyl halide in their reaction with **1** or **2**, (20) although the synthetic utility of this chemistry has not been explored.

3.4. Methylenation of Ketones and Aldehydes

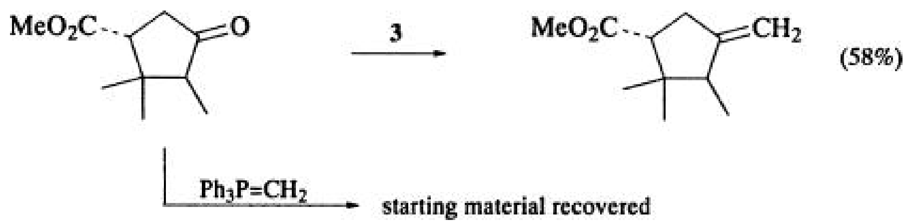
The principal use of these titanium reagents has been for the methylenation of ketones and aldehydes, a process that duplicates the classical Wittig procedure with methylenetriphenylphosphorane. Reagents **1**, **2**, and **3** have shown general utility with a large variety of structures. Reagent **3** has had the broadest range of applications with ketones and aldehydes since it does not react with esters and appears to be more tolerant than **1** or **2** toward the presence of other functional groups. The reagents generally react more rapidly than the analogous Wittig reagent and have proven particularly useful for transformations that cannot be accomplished satisfactorily by the Wittig reaction.



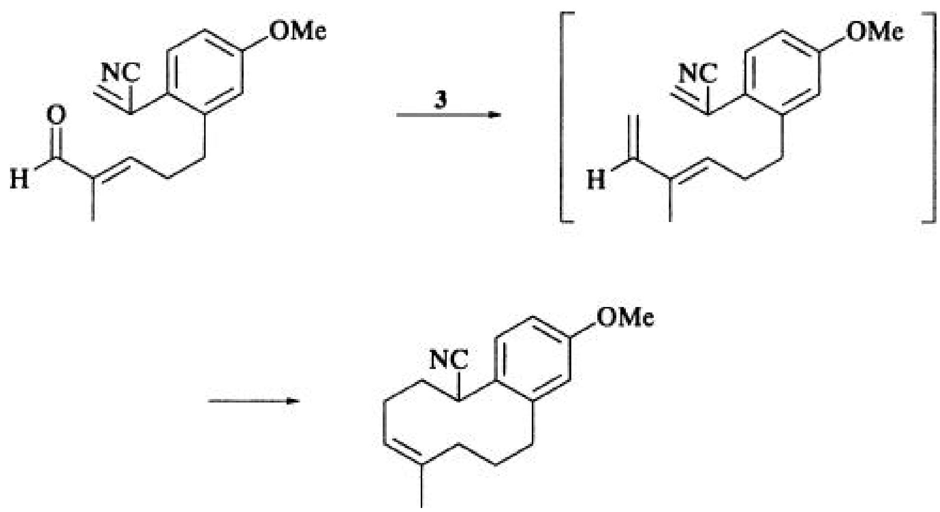
Steric hindrance is one of the factors that severely limits the Wittig methylenation. (7, 74, 75) In a study that compared the effectiveness of **1** with methylenetriphenylphosphorane for ketone methylenation, it was found that the titanium reagent is markedly superior to the Wittig reagent when the carbonyl group is hindered. (23)



The basic nature of Wittig reagents and most of the processes that involve an elimination step to accomplish alkylidenation (5, 7, 76) can limit effective reaction with enolizable ketones. This problem is commonly associated with the acidity of the substrate or with steric hindrance that inhibits reaction at the carbonyl. (57) By contrast the titanium reagents have proven particularly effective for the methylenation of enolizable ketones. (24, 27, 77-82)



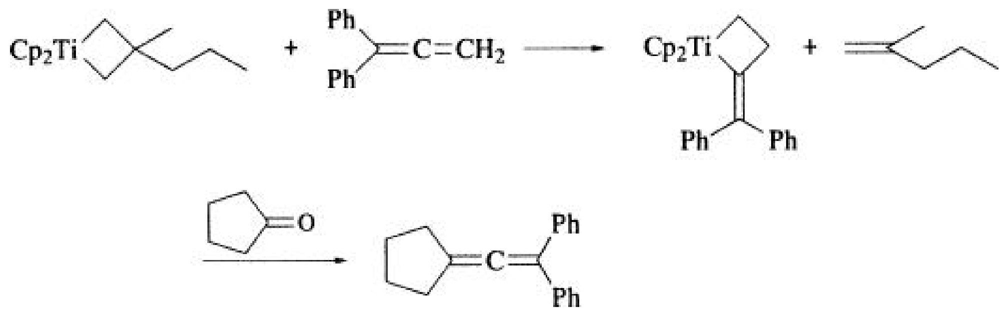
Methylenation of aldehydes has been carried out using all of the titanium reagents discussed above. In one example, reaction of **3** with an unsaturated aldehyde proceeded through a diene that underwent a Diels–Alder cyclization. (62)



3.5. Alkylidenation of Ketones

A significant limitation to the use of the titanium reagents **1**, **2**, and **3** is that they only accomplish methylenation of a ketone. Attempts to form higher homologs of the titanium–aluminum metallacycle following the synthesis model for **1** are not successful. This has been attributed to decomposition by β -hydride elimination. (30, 83) Homologs of **1** have been prepared by hydroalumination of an alkenyltitanium, (30) hydrotitanation of an alkenylalane, (84) methyltitanation of an alkynylalane, (85) and from a divinyltitanocene. (86) These potential reagents for carbonyl alkylidenation have not yet been used in synthesis.

A clever approach to alkylidenation involves exchange of one alkylidene group of the titanium metallacycle for another using an allene, and then allowing the new metallacycle to alkylidenate a ketone. (87) A new allene is formed.

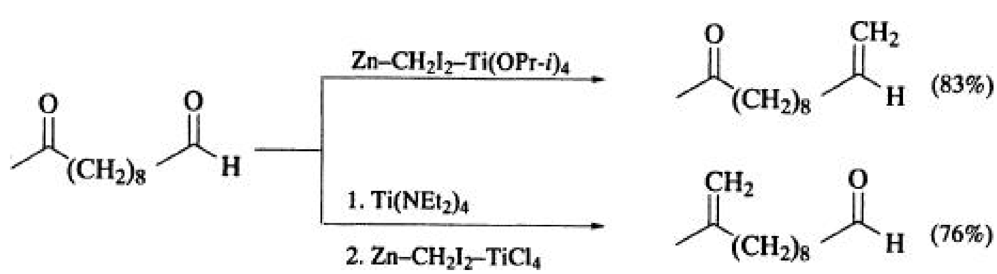


Although alkylidenation of esters and amides has been accomplished through the modified reagent **5** generated from a 1,1-dihalo compound, there are no published reports of similar alkylidenation being carried out with aldehydes or ketones. (88)

3.6. Functional Group Selectivity

Reagents **1** and **2** methylenate the carbonyl group of aldehydes, ketones, esters, and amides. Ketones and amides react with **1** more rapidly than esters so that it is often possible to selectively methylenate only one functional group. (12, 89) However, the reactivity differences are not great, and unless a functional group is hindered, (66, 89) it may be advisable to protect one of the groups while the other undergoes reaction. Reagent **1** reacts with acidic hydrogens such as those on alcohols or carboxylic acids, and those functional groups usually should be protected.

Reagent mixture **3** is selective for ketones and aldehydes, hence methylenation is effective in the presence of esters. (77, 90-95) and hydroxy groups. (96-99) An interesting modification of **3** allows selective reaction of an aldehyde in the presence of a ketone by using $Ti(OPr\text{-}i)_4$ instead of $TiCl_4$. (51) Furthermore, reaction of a ketone in the presence of an aldehyde can be accomplished by first complexing the aldehyde carbonyl with $Ti(NEt_2)_4$, then using reagent **3**. (51)



Reagent **1** reacts with carbon–carbon double bonds to form metallacycles, (25) but at a rate that is slower than its reaction with a carbonyl group. Although there is the potential for interaction of **1** with a double bond in the substrate that could lead to *E-Z* or positional isomerization, this has generally not been a problem. (10, 12) A few examples of positional isomerization have been reported (100-102) but appear to be due to residual metals or the presence of a proton source.

4. Other Alkylidenation Methods

Direct alkylidenation of the carbonyl group of carboxylic acid derivatives was not a viable synthetic operation prior to the availability of **1**. (21, 22, 103) However, many methods had been developed for alkylidenation of aldehydes and ketones. The most widely used is the Wittig reaction using phosphoranes (1) and related phosphonates. (104, 105) The Wittig method is often unsuccessful when the carbonyl group is sterically crowded, (7, 74, 75, 106) and its basic condition can lead to enolization or epimerization of the substrate. (57, 78, 80) Modifications to the preparation of the phosphorus ylides have minimized some of these problems. (107-110)

A variety of methods have been developed which involve addition of an anionic reagent to the carbonyl carbon, then elimination of the alcohol intermediate. Like the Wittig reaction, most of these involve basic reaction conditions and can result in enolization. These anionic reagents include trimethylsilylmethylmagnesium chloride, (5) trimethylsilylmethyllithium, (111) trimethylsilylmethyllithium–cerium trichloride, (112) trimethylsilylbenzyllithium, (113) phenylthiomethyllithium, (7) triphenylstannylmethyllithium, (6) sodium phenylselenide, (114) 1-lithioalkyldimethylphosphonothionates, (76) lithioalkylphenylphosphinothioic amides, (8) and methylphenylsulfonimidoylmethyllithium. (115)

5. Reaction Conditions

The Tebbe reagent **1**, a deep red moisture-sensitive solid, can be prepared in advance of its use (9) since it is stable indefinitely as a dry solid or as a homogeneous solution in toluene or benzene. It it available commercially and is usually used in stoichiometric quantities.

In situ methods for preparation of the reagent have also been developed to simplify its use, (72, 100, 116, 117) although yields of the methylenation product are generally lower than those obtained by using the pure reagent. The metallacyclic analogs **2** of **1** are prepared from **1** (25) and are reported to be more air stable than **1**. They usually must be heated to provide the active alkylidene. Their use in synthesis has been rather limited.

Because of its sensitivity to moisture, **1** is handled by common inert atmosphere techniques. (118) Solvents and apparatus should be dry. Solvents are usually dried and freed of oxygen by distillation from sodium–benzophenone ketyl. (119) In some reactions, base washing of apparatus to remove acid residues has led to enhanced yields. (100)

Reagent mixture **3** (and **5**) is normally prepared in situ as needed for use. It is a dark viscous material that is only partially soluble in the solvents usually used for reaction (tetrahydrofuran and dichloromethane). Methods involving a three-day preparation (28) or a 15 to 30-minute preparation (11) are both in general use, although the longer period is reported to provide better results. (28) The methylene reagent **3** slowly decomposes at room temperature but can be stored for up to one year at –20°. (28) Reactions are usually carried out using stoichiometric amounts of titanium tetrachloride relative to the carbonyl compound with excess zinc and dihalomethane. (28) In some cases large excesses of all reagents relative to the carbonyl are needed to provide good yields. (82, 120, 121) The zinc is usually activated by washing with hydrochloric acid (28, 122) and in some cases purity of the zinc (16) and titanium tetrachloride (92) has proven important for good yields of product. Dry solvents and an inert atmosphere are used.

Purification of most of the products of these reactions involves chromatography to separate the inorganic residues from the organic product. Enol ethers may undergo hydrolysis or isomerization during chromatography by an acid-catalyzed mechanism. In this case, product stability is often enhanced by using basic alumina, and in some examples the eluent is saturated with trimethylamine. (12)

All of the titanium reagents mentioned above react with moisture. Residues from the reaction procedures can usually be destroyed by careful quenching with acetone. Aluminum-containing residues react more vigorously and are better destroyed with butanol.

6. Experimental Procedures

*6.1.1.1. (5'-tert-Butyl-1'-cyclohexenyl)methyl 2-(1-Butenyl) Ether (Methylenation of an Ester Using the Tebbe Reagent **1**) (60)*

To a solution of 0.303 g (1.34 mmol) of 5-*tert*-butyl-1-cyclohexenylmethyl propanoate in 3 mL of THF cooled to –40° was added 4.5 mL of a 0.33 M solution (1.48 mmol) of Tebbe reagent in toluene over a period of 3 minutes. After 1 hour at –40°, the reaction mixture was allowed to warm to room temperature and stirred further for 1.5 hours. The reaction was quenched with 0.5 mL of 10% aqueous sodium hydroxide, then diluted with 100 mL of diethyl ether. After drying with anhydrous sodium sulfate and filtering through Celite, the solvent was removed under vacuum. The product was purified by chromatography using alumina (activity III) with hexane as eluent. The enol ether, 0.257 g (86%), was recovered as a colorless oil (bp 60°, 0.1 torr). ^1H NMR ($CDCl_3$) δ 0.88 (s, 9H, $C(CH_3)_3$) , 1.0–2.35 (m, 12H), 3.82 (br s, 2H, CH_2O), 4.05 (br s, 2H C = CH_2), 5.72 (br s, 1H, C = CHC).

*6.1.1.2. 3-Benzyloxy-1-phenyl-1,3-butadiene (Methylenation of a Conjugated Ester Using the Tebbe Reagent **1**) (12)*

To a solution of 0.238 g (1 mmol) of benzyl cinnamate in 2–3 mL of THF at 0° was added 2 mL of 0.5 M Tebbe reagent (1 mmol) in benzene. After 30 minutes, 10–20 mL of ether was added, then 5–10 drops of anhydrous methanol was slowly added. The resulting slurry was filtered through Celite and the filtrate concentrated by rotary evaporation. Purification by chromatography on basic alumina using 2% ether/pentane gave 0.195 g (82%) of product. ^1H NMR (CCl_4) δ 4.2 (s, 2H, ArCH_2), 4.75 (s, 2H, = CH_2), 6.3–7.2 (m, 2H, CH = CH), 7.0–7.4 (m, 10H, Ar-H).

*6.1.1.3. 1-Phenoxy-1-phenylethene (Methylenation of an Ester Using the in situ Tebbe Reagent **1**) (100)*

To a 250-mL round-bottom flask equipped with a magnetic stirrer and an inert gas purge was added 5.0 g (20 mmol) of titanocene dichloride [bis(cyclopentadienyl)titanium dichloride], followed by 20 mL of a solution of 2 M trimethylaluminum in toluene (40 mmol). The resulting red solution was stirred at room temperature for 3 days as methane gas evolved. The resulting solution contains the Tebbe reagent. The solution was cooled in ice water, then 4.0 g (20 mmol) of phenyl benzoate in 20 mL of dry THF was added over 5–10 minutes. The reaction was allowed to warm to room temperature over 30–45 minutes, then 50 mL of anhydrous diethyl ether was added. At this point the inert atmosphere is no longer needed. Approximately 50 drops of 1 M aqueous sodium hydroxide was carefully added over 10–20 minutes. The resulting slurry was stirred until gas evolution ceased (about 20 minutes). Anhydrous sodium sulfate was then added and the slurry passed through a Celite pad on a coarse-frit Büchner funnel. The Celite was rinsed with additional ether, then the solvent was concentrated to a volume of 5–8 mL using a rotary evaporator. The crude product was purified by column chromatography on basic alumina (150 g) eluting with 10% ether in pentane. Evaporation of the product-containing fractions provided 2.8 g (70%) of the desired enol ether. ^{1}H-NMR (250 MHz, $CDCl_3$) δ 4.45 (d, 1H, *J* = 2.3 Hz, = CH), 5.05 (d, 1H, *J* = 2.3 Hz, = CH), 7.06–7.11 (m, 3H, Ar-H), 7.29–7.38 (m, 5H, Ar), 7.66–7.70 (m, 2H, Ar-H); IR (neat) 1600, 1495, 1290, 1230 cm_{-1}.

*6.1.1.4. 5-(3¢-Benzyloxypropyl)-1,2-dimethyl-4-methylene-3,9-dioxabicyclo-[4.2.1]nonane (Methylenation of a Lactone Using the Tebbe Reagent **1**) (123)*

A solution of 4.5 g (14.2 mmol) of the bicyclic ketone 5-(3¢-benzyloxypropyl)-1,2-dimethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one in 57 mL of anhydrous THF was cooled to –45°. To this solution was added 0.7 mL of freshly distilled pyridine followed by a cooled solution (–45°) of 6.1 g (19.3 mmol) of Tebbe's reagent in 28 mL of toluene. The reaction was maintained at –45° for 40 minutes and then allowed to warm to 20° over 2 hours. After an additional 45 minutes, the red solution was cooled to 0° and 6 mL of 15% aqueous NaOH was carefully added. After 1 hour, 60 mL of ether was added and the resulting slurry was filtered through 300 g of neutral alumina (activity III) with 1 L of hexane followed by 500 mL of ether. Evaporation of the solvent in vacuo afforded 4.2 g (94%) of product as a yellow oil. ^{1}H NMR (90 MHz, CCl_4) δ 1.05 (s, 3H, CH_3), 1.11, (d, 3H, *J* = 7 Hz, $OCHCH_3$), 1.2–2.3 (m, 8H), 2.66 (q, 1H, *J* = 6 Hz, allylic CH), 3.33 (t, 2H, *J* = 6 Hz, $PhCH_2OCH_2$), 3.56 (q, 1H, *J* = 7 Hz, OCH-CH_3), 4.20 (m, 1H, tetrahydrofuranyl CH), 4.22 (s, 1H, vinyl CH), 4.38 (s, 2H, $PhCH_2O$), 4.48 (s, 1H, vinyl CH), 7.21 (s, 5H, Ar-H).

*6.1.1.5. 3,4-Dihydro-2-methylene-2H-1-benzopyran (Methylenation of a Lactone Using the in situ Tebbe Reagent **1**) (100)*

To a 250-mL round-bottom flask equipped with a magnetic stirrer and an inert gas purge was added 5.0 g (20 mmol) of titanocene dichloride [bis(cyclopentadienyl)titanium dichloride], followed by 20 mL of a solution of 2 M trimethylaluminum in toluene (40 mmol). The resulting red solution was stirred at room temperature for 3 days as methane gas evolved. The resulting solution contains the Tebbe reagent. The solution was cooled in dry ice–acetone, then 3.0 g (20 mmol) of dihydrocoumarin in 20 mL of dry THF was added over 5–10 minutes. The solution was allowed to warm to room temperature over 30–45 minutes, then 50 mL of anhydrous diethyl ether added. At this point the inert atmosphere is no longer needed. Approximately 50 drops of 1 M aqueous sodium hydroxide was carefully added over 10–20 minutes. The resulting slurry was stirred until gas evolution ceased (about 20 minutes). Anhydrous sodium sulfate was then added and the slurry passed through a Celite pad on a coarse-frit Büchner funnel. The Celite was rinsed with additional ether, then the solution was concentrated to a volume of 5–8 mL using a rotary evaporator. The crude product was purified by column chromatography on basic alumina (150 g) eluting with 10% ether in pentane. Evaporation of the product-containing fractions provided 1.9 g (67%) of the enol ether. ^{1}H NMR (250 mHz, $CDCl_3$), δ 2.57 (t, 2H, J = 6.5 Hz, -CH_2), 2.80 (t, 2H, J = 6.5 Hz, Ar-CH_2), 4.14 (s, 1H, =CH), 4.55 (s, 1H, = CH), 6.85–6.92 (m, 2H, Ar-H), 7.03–7.07 (m, 1H, Ar-H), 7.11–7.18 (m, 1H, Ar-H); IR (neat) 1665, 1595, 1500, 1470, 1250, 990, 770 cm^{-1}.

*6.1.1.6. 2-Methoxy-1-trimethylsilyl-1-tridecene (Alkylidenation of an Ester Using a Modified Takai Reagent **5**) (26)*

To a solution of 15 mL of THF and 6 mL of CH_2Cl_2 at 0° was added a solution of 2 mL of 2 M $TiCl_4$ in CH_2Cl_2 (4 mmol). The yellow solution was warmed to 25° then 1.2 mL (8 mmol) of TMEDA was added and the mixture was stirred for 15 minutes. Zinc dust (0.57 g, 9.0 mmol) was then added and the mixture was stirred for 30 minutes. A solution of 0.198 g (1.0 mmol) of methyl dodecanoate and 0.54 g (2.2 mmol) of dibromotrimethylsilylmethane in 1 mL of CH_2Cl_2 was added to the reagent mixture. After the reaction mixture was stirred for 3 hours at 25°, 10 mL of THF was added and the mixture was cooled to 0°. A solution of 2 mL of saturated aqueous sodium carbonate was added, and the mixture was stirred at 0° for 1 hour. The mixture was diluted with 10 mL of 200:1 ether/triethylamine and then passed rapidly through a short column of basic alumina (activity III). The resulting solution was concentrated and the solid filtered through Hyflo Super-Cel using 50 mL of 200:1 hexane/Et_3N as eluent. Concentration of the filtrate followed by chromatography on basic alumina (activity III) using 200:1 hexane/ Et_3N and evaporation of the solvent gave 0.246 g (92%) of a mixture of isomers. ^{1}H NMR ($CDCl_3$) δ 0.05 [s, 9H, $Si(CH_3)_3$] , 0.88 (t, 3H, J = 7 Hz, CH_3), 1.20–1.70 (m, 18H), 2.16 (t, 2H, J = 7 Hz, CH_2C =), 3.48 (s, 3H, E-OCH_3), 3.51 (s, 3H, Z-OCH_3), 4.00 (s, 1H, E- = CH), 4.30 (s, 1H, Z- = CH).

*6.1.1.7. 4-Phenyl-1-methylidenecyclohexane (Methylenation of a Ketone Using the in situ Tebbe Reagent **1**) (116)*

To a 250-mL round-bottom flask equipped with a magnetic stirrer and an argon purge was added 12.45 g (50 mmol) of titanocene dichloride. A solution of 2 M trimethylaluminum in toluene (55 mL, 110 mmol) was transferred into this flask via cannula from an argon-purged graduated cylinder. The resulting red solution was stirred at room temperature as methane evolved. After 72 hours, an additional 20 mL of 2 M trimethylaluminum in toluene was added (a total of 150 mmol of trimethylaluminum) and stirring was continued for an additional 12 hours. To a 500-mL round-bottom flask equipped with an argon purge and magnetic stirrer was added 11.3 g (65 mmol) of 4-phenylcyclohexanone and 80 mL of dry THF. This solution was cooled to –40°, then the previously prepared in situ Tebbe reagent was added via cannula over 10 minutes while maintaining the temperature at or below –40°. Stirring was continued for 0.5 hour at –40°, for 1.5 hours at –40 to 0°, and for 1 hour at room temperature. Reagent grade THF (50 mL) was added and the resulting mixture cooled to

–10°. An aqueous solution of 15% sodium hydroxide was added slowly while the mixture was maintained at –10°. As methane evolution slowed, the sodium hydroxide solution was added more rapidly, and stirring or swirling was continued with the viscous mixture. The mixture was filtered using a coarse-frit Büchner funnel, washing the residue with ether. The solvent was removed using a rotary evaporator, and the resulting toluene solution of the product was diluted with 300 mL of pentane. The resulting slurry was filtered as described above and the residue was washed with additional pentane. Removal of the solvent followed by reduced pressure distillation afforded 9.2 g (82%) of product (bp 88°, 2 torr). ^{1}H NMR (CD_2Cl_2) δ 1.45–2.89 (m, 9H, ring), 4.72 (m, 2H, = CH_2), 7.26 (m, 5H, Ar-H); ^{13}C NMR (CD_2Cl_2) δ35.7, 36.1, 44.6 107.6, 126.4, 127.3, 128.8, 147.5, 149.4.

*6.1.1.8. 2,6-Dimethylmethylidenecyclohexane (Methylenation of a Hindered Ketone Using the Tebbe Reagent **1**) (23)*

To a solution of 0.126 g (0.001 mol) of 2,6-dimethylcyclohexanone in 2–3 mL of THF at 0° was added a solution of 2 mL of 0.5 M Tebbe reagent in benzene (0.001 mol). The solution was allowed to warm to room temperature over a period of 30 minutes. Ether (15–20 mL) was added, followed by careful addition of 5–10 drops of 0.1 M aqueous NaOH. After the gas evolution ceased, the solution was dried with anhydrous sodium sulfate, then filtered through a pad of Celite. Rotary evaporation of the solvent provided the crude product which was then purified by chromatography using neutral alumina with an eluent of 2% ether in petroleum ether (40–60°). Evaporation of the solvent gave 0.120 g (97%) of product. ^{1}H NMR (CCl_4, 90 MHz) δ 1.0 (d, 6H, J = 6 Hz, CH_3), 1.3–2.2 (m, 8H, ring), 4.5 (s, 2H, vinyl CH_2).

*6.1.1.9. 3-Methylene-p-menthane (Methylenation of a Ketone Using the Lombardo Modification **3**) (28)*

To a 1-L round-bottom flask with a magnetic stirrer, pressure-equalizing dropping funnel, and nitrogen purge was added 28.75 g (0.44 mol) of activated zinc powder, (122) 250 mL of dry THF, and 10.1 mL (0.144 mol) of dibromomethane. The mixture was stirred and cooled to –40°, then 11.5 mL (0.103 mol) of titanium tetrachloride was added over 15 minutes. The mixture was then stirred for 3 days at 5°. The resulting slurry was cooled to 0° and 50 mL of dry dichloromethane added. To this mixture at 0° was added 15.4 g (0.1 mol) of isomenthone over 10 minutes. The reaction mixture was stirred at 20° for 1.5 hours. The mixture was then diluted with 300 mL of pentane and a slurry of 150 g of sodium bicarbonate in 80 mL of water was added carefully over 1 hour. The organic layer was decanted into a 1.5-L flask and the residue was washed with three 50-mL portions of pentane. The combined organic solution was dried with 100 g of anhydrous sodium sulfate and 20 g of sodium bicarbonate. The organic solution was recovered by filtration and the solvent was removed by flash distillation. The residue was distilled under reduced pressure to give 13.6 g (89%) of product (bp 105–107°, 90 torr). ^{1}H NMR

($CDCl_3$, 200 MHz) δ 0.79 (d, 3H, *J* = 7 Hz, - CH_3), 0.91 (d, 6H, *J* = 7 Hz, - CH_3), 1.01–2.14 (m, 9H, - CH, ring - CH_2), 4.54 (s, 1H, =CH), 4.60 (s, 1H, - CH); ^{13}C NMR ($CDCl_3$) δ 17.4, 18.3, 19.2, 22.6, 25.8, 26.5, 31.8, 37.3, 47.4, 104.6, 148.4.

6.1.1.10. 2-(tert-Butyldimethylsiloxy)-4a-methyl-3-(1-methylethylidene)-5-methylene-3,4,4a,5,6,7,8,8a-octahydronaphthalene (Methylenation of a Hindered Ketone Using the Lombardo Modification ***3****) (82)*

To a solution of 0.174 g (0.52 mmol) of 6-(*tert*-butyldimethylsiloxy)-8a-methyl-7-(1-methylethylidene)-3,4,4a,7,8,8a-hexahydro-1(2*H*)-naphthalenone in 15 mL of CH_2Cl_2 at room temperature was added reagent **3** (28) prepared from 0.601 g (9.2 mmol of zinc dust, 7 mL of THF, 0.22 mL (3.1 mmol) of CH_2Br_2, and 0.24 mL (2.2 mmol) of $TiCl_4$. The mixture was stirred for 45 minutes, then several milliliters of triethylamine was added followed by saturated aqueous sodium bicarbonate. The organic layer was washed with 15 mL of brine and dried over sodium sulfate, and the solvent was evaporated. The crude product was purified by preparative TLC on a Chromatotron with 10% ether/pentane. The first band to elute gave, after evaporation, 0.162 g (94%) of product as a 2:1 mixture of isomers. ^1H NMR ($CDCl_3$, 200 MHz) δ 0.10, 0.15 (2 s, 6H), 0.89, 0.95, 1.10 (3 s, 12H), 1.18–2.65 (m 15H), 4.52–4.72 (m, 3H).

6.1.1.11. 8-tert-Butyldimethylsilyloxy-1-[(2-methoxyethoxy)methoxy]-4-methylene-1 α ,2,3,3a α ,4,5,8 β ,8a α -octahydroazulene (Methylenation of an Enolizable Ketone Using the Lombardo Modification ***3****) (124)*

To a stirred solution of 0.576 g (1.47 mmol) of 8-[(*tert*-butyldimethylsilyl)oxy]-1-[(2-methoxyethoxy)methoxy]-1 α ,2,3,3a α ,8 β ,8a α -hexahydroazulen-4(5*H*)-one in 3 mL of methylene chloride was added Lombardo's reagent (28) in small portions via a pipet. The reaction was monitored by TLC, and when the starting material had been consumed the reaction mixture was diluted with 100 mL of ether. The ether mixture was shaken with 100 mL of saturated aqueous sodium bicarbonate until the organic layer was clear, then the aqueous phase was backwashed with several 100-mL portions of ether. The combined organic layers were dried over anhydrous sodium sulfate and evaporated under reduced pressure to give crude product. Flash chromatography on 20 g of silica gel (1:3 ether/hexanes) gave pure product: 0.557 g (99%). ^1H NMR (CCl_4) δ 0.01 [s, 6H, $Si(CH_3)_2$], 0.85 [s, 9H, $SiC(CH_3)_3$], 1.49 (m, 1H), 1.88 (m, 1H), 2.04–2.28 (m, 2H), 2.33 (dd, 1H, *J* = 4.0, 11.0 Hz), 2.68 (m, 1H), 2.82 (m, 1H), 3.03 (dddd, 1H, *J* = 2.7, 2.7, 2.7, 18.6 Hz), 3.42 (s, 3H, OCH_3), 3.59 (m, 3H), 3.90 (m, 1H), 4.00 (m, 1H), 4.75 (m, 3H), 4.97 (br s, 1H, = CH_2), 5.00 (br s, 1H, = CH_2), 5.31 (dddd, 1H, *J* = 2.7, 2.7, 5.2, 11.6 HZ, C = CH), 5.56 (m, 1H, C = CH).

6.1.1.12. trans-3,4-Diphenyl-1-methylidenecyclopentane (Methylenation of a Ketone Using the Takai Reagent ***3*** *Prepared from Diiodomethane) (125)*

To a well-stirred suspension of 9.95 g (152 mmol) of zinc dust in 175 mL of THF was added 6.8 mL (84.6 mmol) of diiodomethane. The resulting slurry was stirred at room temperature for 30 minutes. It was cooled to 0° and 17 mL of 1.0 M $TiCl_4$ in CH_2Cl_2 (170 mmol) was slowly added and the slurry stirred for 30 minutes. A solution of 4.0 g (17 mmol) of *trans*-3,4-diphenylcyclopentanone in 20 mL of THF was added dropwise. After 2.5 hours the reaction was diluted with ether, washed with 1 M aqueous HCl, and then saturated NaCl, and the organic phase was dried with magnesium sulfate. Concentration of the product followed by chromatography on 250 g of silica gel 60 using 10% ethyl acetate/hexanes as eluent gave 3.66 g (92%) of the pure product as a pale yellow oil. ^{1}H NMR ($CDCl_3$) δ 2.54–2.70 (m, 2H, ring), 2.85–2.98 (m, 2H, ring), 3.15–3.30 (m, 2H, Ar-CH), 4.92–4.98 (m, 2H, = CH_2), 7.02–7.22 (m, 10H, Ar-H).

*6.1.1.13. 3,3-Dimethyl-1,1-diphenyl-1,4-pentadiene (Alkylidenation of a Ketone with a Metallacycle **2**) (44)*

To a 1-mL toluene solution of 0.050 g (0.19 mmol) of the metallacycle prepared from **1** and 3,3-dimethylcyclopropene was added 0.039 g (0.21 mmol) of benzophenone at 0°. The reaction mixture was warmed to 23°, stirred for 10 hours, and then diluted with 10 mL of petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel and the solvent evaporated to give 0.040 g (83%) of colorless oil. ^{1}H NMR (CCl_4) δ 1.06 [s, 6H, $C(CH_3)_2$], 4.69 (dd, 1H, *J* = 12 Hz, 1.5 Hz, = CH), 4.83 (dd, 1H, *J* = 18 Hz, 1.5 Hz, = CH), 5.77 (dd, 1H, *J* = 18 Hz, 12 Hz, - CH =), 6.03 (s, 1H, = CH -), 7.16 (m, 10H, Ar-H).

7. Tabular Survey

The tables include methylenation and alkylidenation reactions found by computer searching of the literature through September 1990. Each table reflects the type of substrate (ester, aldehyde, or ketone) and the type of reaction (methylenation or alkylidenation). The tables of esters include lactones, thioesters, and silyl esters. Table entries are arranged by increasing number of carbon atoms in the substrate. Protecting groups such as silyl esters and acetals are not included in the carbon count. In some entries, data from substrates reflecting a series of structural changes are grouped together and entered by the carbon number of the parent structure.

Where available, reaction conditions are those reported in the experimental section of the literature article. However, many table entries were obtained from short communications in which experimental procedures were not included. In those cases the experimental method referred to in the table is assumed to be that which was referenced in the report. The symbol (—) indicates that no yield was reported.

In the Conditions column, the symbol >C = O indicates the point in the reaction sequence at which the carbonyl compound was added.

The following abbreviations are used in the tables:

Bn	benzyl
Cp	cyclopentadienyl
DMAP	*p*-dimethylaminopyridine
DMTMPS	Dimethyl(1,1,2-trimethylpropyl)silyl
Et_2O	diethyl ether
MEM	methoxyethoxymethyl
MOM	methoxymethyl
Pyr	pyridine
SEM	(2-trimethylsilylethoxy)methyl
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
Tebbe	Tebbe reagent (**1**)
TES	triethylsilyl
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMEDA	*N*,*N*,*N′*,*N′*-tetramethylethylenediamine

TMS	trimethylsilyl
Tol	toluene
Ts	*p*-toluenesulfonyl

Table I. Methylenation of Esters

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Table II. Methylenation of Ketones

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Table III. Methylenation of Aldehydes

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Table IV. Methylenation of Amides

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Table V. Alkylidenation of Esters

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Table VI. Alkylidenation of Ketones and Aldehydes

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Table VII. Alkylidenation of Amides

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Table I. Methylenation of Esters

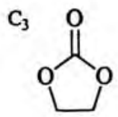
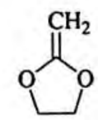
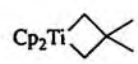
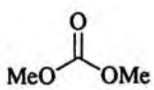
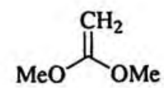
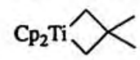
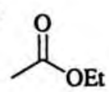
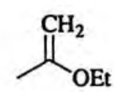
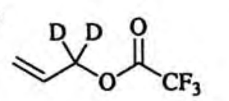
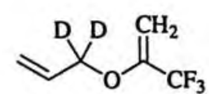
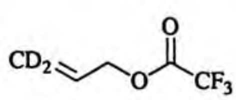
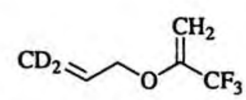
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (56)	15
		" (56)	15
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (60)	15
		" (60)	15
C_4 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	9
C_5 	$TiCl_4$, CH_2Br_2, diglyme, TMEDA, >C=O, rt, 4.5 h	 (—)	13
	$TiCl_4$, CH_2Br_2, diglyme, TMEDA, >C=O, rt, 4.5 h	 (—)	13

Table I. Methylenation of Esters (*Continued*)

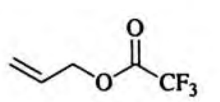
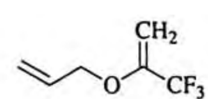
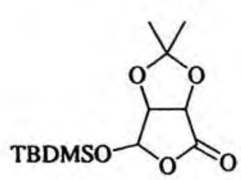
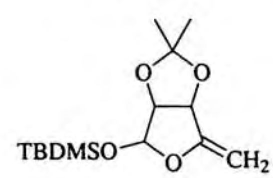
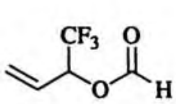
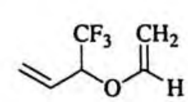
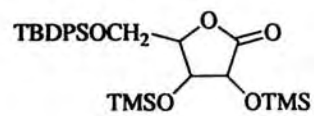
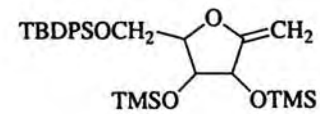
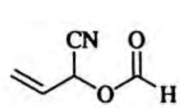
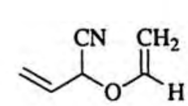
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$TiCl_4$, CH_2Br_2, diglyme, TMEDA, >C=O, rt, 4.5 h	 (—)	13
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (85)	126
	1. Tebbe, Tol 2. >C=O, THF, Tol. Pyr, -40° 3. -40°, 30 min; rt, 90 min	 (—)	13
	1. Tebbe, Tol 2. >C=O, THF, Tol. Pyr, -40° 3. -40°, 30 min; rt, 90 min	 (68)	127
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	128

Table I. Methylenation of Esters (*Continued*)

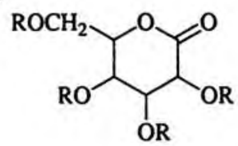
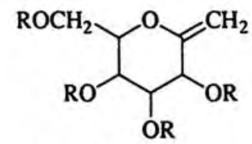
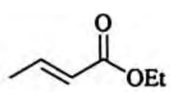
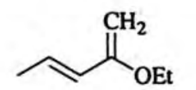
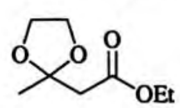
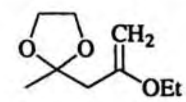
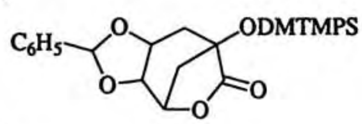
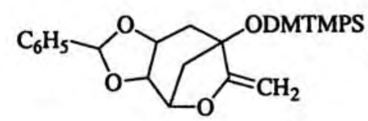
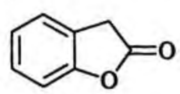
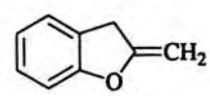
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	1. Tebbe, Tol 2. >C=O, THF, Tol. Pyr, -40° 3. -40°, 30 min; rt, 25 min	 R = Bn (82) R = TMS (54) R = TES (86)	127
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (82)	10
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (87)	10
C_7			
	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, CH_2Br_2, THF, 25°, 2 h	 (74)	64
C_8			
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (85)	10, 12

Table I. Methylenation of Esters (*Continued*)

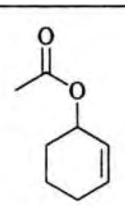
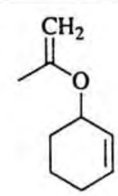
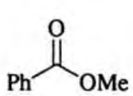
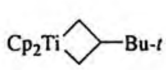
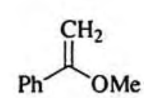
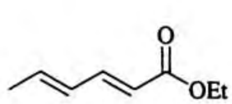
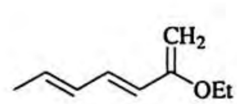
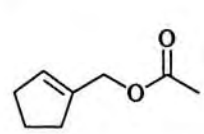
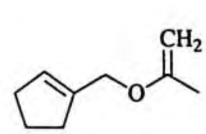
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63
		 (90)	129
	1. $Cp_2Ti(Cl)CH{=}CHCH_3$, $HAl(Pr\text{-}i)_2$, Tol, -40° 2. >C=O	" (—)	30
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (54)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63

Table I. Methylenation of Esters (*Continued*)

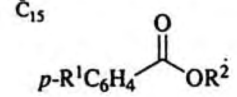
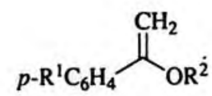
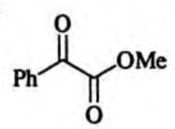
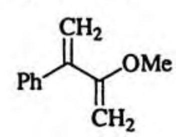
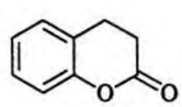
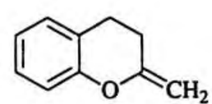
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{15} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min		
		R^1 R^2	
		H Me (81)	12
		Cl Me (76)	12
		Me Me (93)	12
		MeO Me (80)	12
		H CH_2CF_3 (—)	130
		H $(CH_2)_2Cl$ (—)	130
		H Et (—)	130
		H *i*-Pr (88)	12
		H $CH_2CH=CH_2$ (50)	12
		H *t*-Bu (57)	12
		H Ph (84)	12
C_9 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (45)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (85)	10, 12

Table I. Methylenation of Esters (*Continued*)

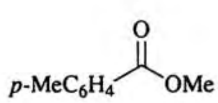
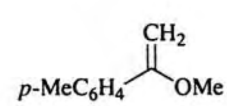
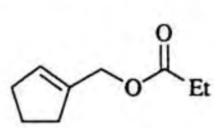
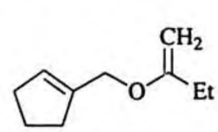
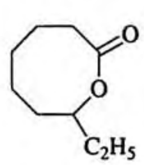
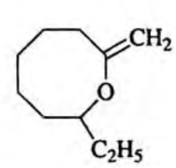
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cp_2TiMe_2, Tol, >C=O, 65° 12-26 h (dark)	" (80)	131
	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, -40°, 30 min; 0°, 1.5 h; rt 1 h	" (76)	116
	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, 0°; rt 45 min	" (67)	100
	$Cl_2AlCH_2TiCl_3$, THF, heat 30 min	 (30)	52
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63
	1. Tebbe, Tol 2. >C=O, THF, Tol, DMAP, -40° 3. -40°, 30 min; rt, 90 min	 (—)	132

Table I. Methylenation of Esters (*Continued*)

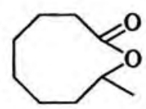
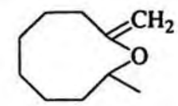
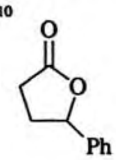
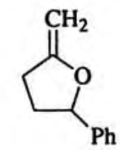
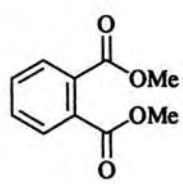
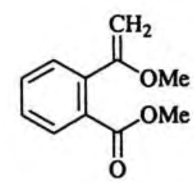
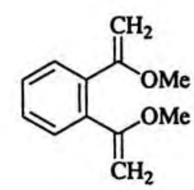
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, DMAP, -40 to 25°	 (—)	133
C_{10}			
	Cp_2TiMe_2, Tol, >C=O, 65° 12-26 h (dark)	 (41)	131
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (45)	12
	1. Tebbe (2 eq), Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (65)	12

Table I. Methylenation of Esters (*Continued*)

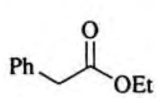
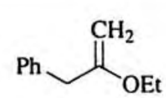
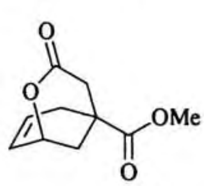
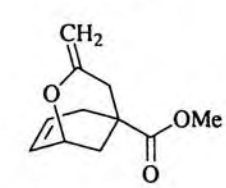
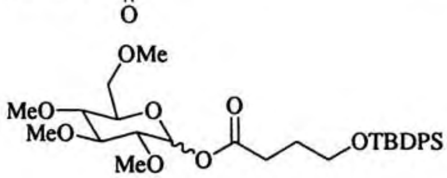
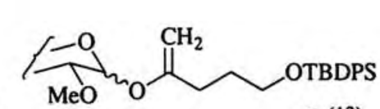
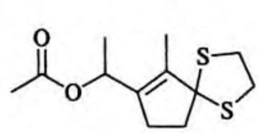
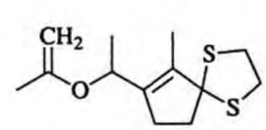
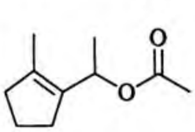
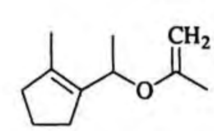
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (90)	10,12
	1. Tebbe, CH_2Cl_2 2. >C=O, -40°	 (—)	57
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 α (13) β (63)	134
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63

Table I. Methylenation of Esters (*Continued*)

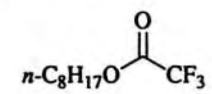
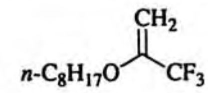
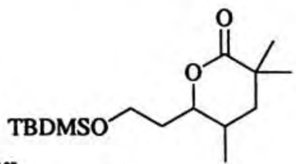
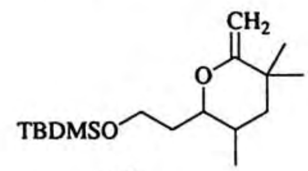
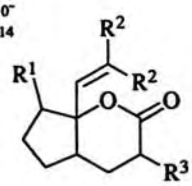
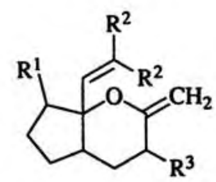
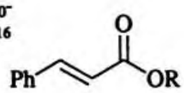
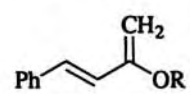
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, CH_2Br_2, rt, 3 h	 (28)	13
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (76)	135
C_{10}-C_{14} 	1. Tebbe, Tol 2. >C=O, THF, Pyr, 0° 3. 25°, 90 min	 R[1] R[2] R[3] H H H (92) Me Me H (—) Me H Me (—) Me Me Me (—)	61
C_{10}-C_{16} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 R = Me (99) R = Et (96) R = Bn (82)	12 10 12

Table I. Methylenation of Esters (*Continued*)

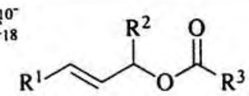
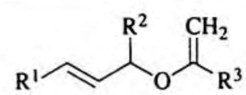
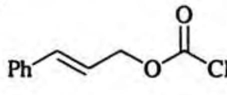
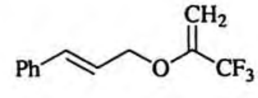
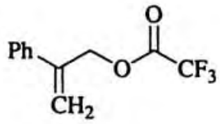
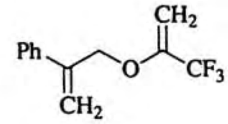
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}-C_{18} 	1. Tebbe, Tol 2. >C=O, THF, Tol, Pyr, -40° 3. rt, 12 h	 R[1] R[2] R[3] H Me Ph (—) Me H Ph (72) *n*-Pr H *i*-Pr (—) *n*-Pr H Ph (—) $Ph(CH_2)_2$ H H (—) $Ph(CH_2)_2$ H Me (—) $Ph(CH_2)_2$ H Ph (—)	59
C_{11} 	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, CH_2Br_2, rt, 3 h	 (53)	13
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, CH_2Br_2, rt, 3 h		13

Table I. Methylenation of Esters (*Continued*)

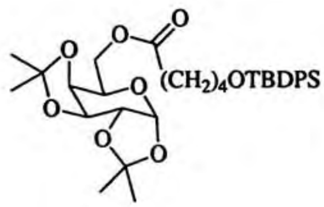
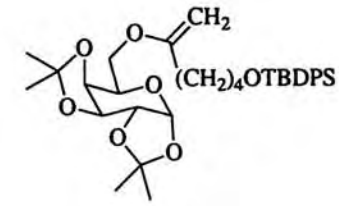
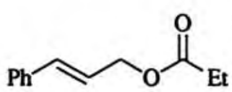
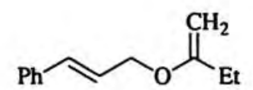
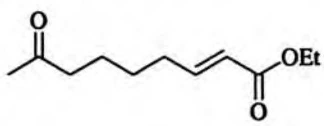
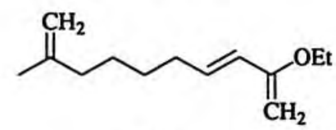
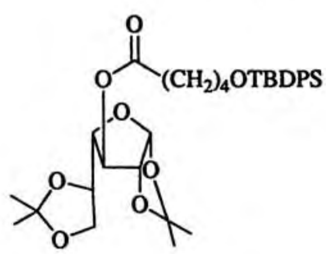
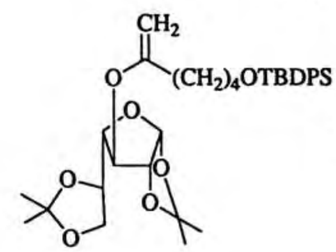
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 (44)	134
 88	1. Tebbe, Tol 2. >C=O, THF, Tol. Pyr, -40° 3. -40°, 30 min; rt, 90 min	 (40)	58
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (81)	10
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 (83)	134

Table I. Methylenation of Esters (*Continued*)

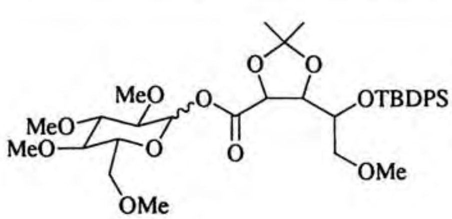
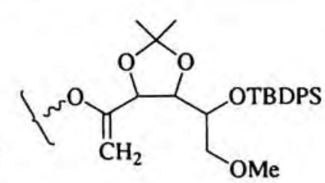
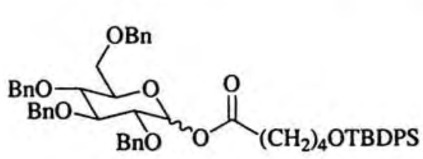
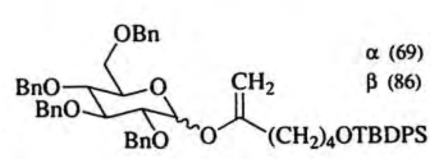
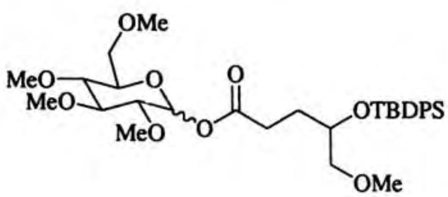
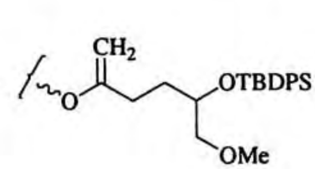
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 α (84) β (72)	134
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 α (69) β (86)	134
	1. Tebbe, Tol 2. >C=O, Tol, Pyr, -40° 3. -40°, 30 min; 0°, 2 h, rt, 1 h	 α (82) β (67)	134

Table I. Methylenation of Esters (*Continued*)

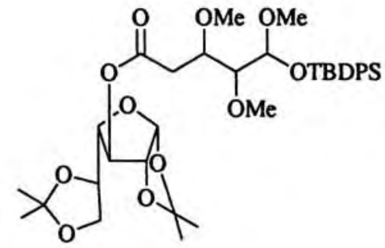
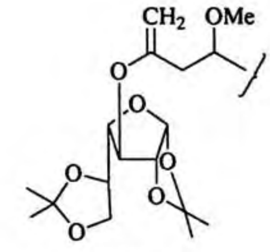
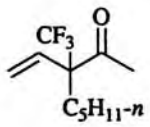
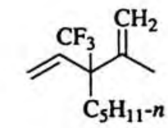
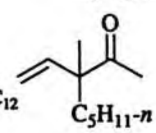
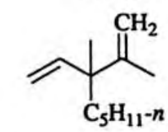
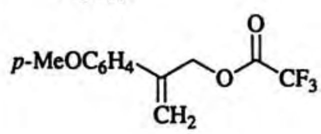
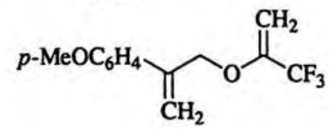
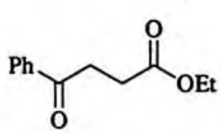
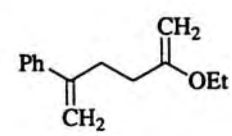
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, Tol, Pyr, -40° 3. -40°, 30 min; rt, 1 h	 (82)	134
	1. Tebbe, Tol 2. >C=O, THF, Tol, Pyr, -40° 3. -40°, 30 min; rt, 1 h	 (10)	13
C_{12} 	1. Tebbe, Tol 2. >C=O, THF, Tol, Pyr, -40° 3. -40°, 30 min; rt, 1 h	 (—)	13
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, CH_2Br_2, rt, 3 h	 (8)	13
	1. Tebbe (2 eq), Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (97)	10

Table I. Methylenation of Esters (*Continued*)

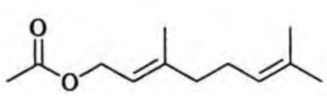
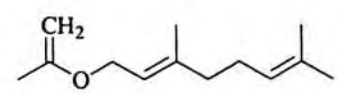
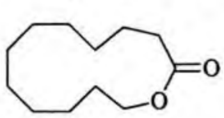
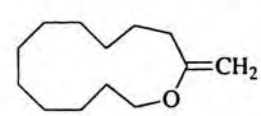
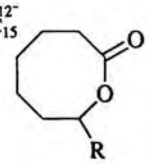
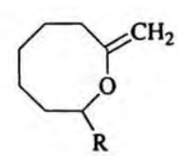
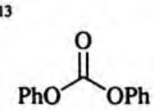
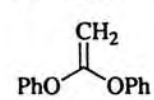
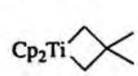
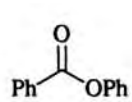
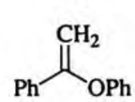
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63
	Cp_2TiMe_2, Tol, >C=O, 65° 12-26 h (dark)	 (70)	131
C_{12}-C_{15} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 R = n-C_5H_{11} (—) R = n-C_6H_{13} (—)	136
C_{13} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (15)	15
		" (15)	15
	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, 0°, rt, 45 min	 (70)	100

Table I. Methylenation of Esters (*Continued*)

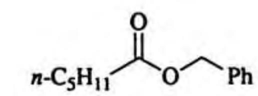
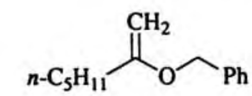
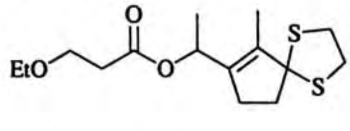
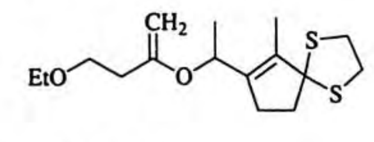
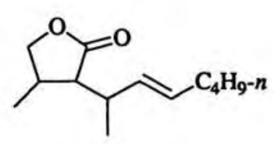
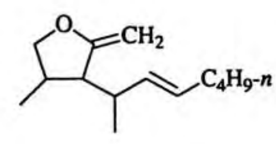
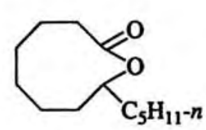
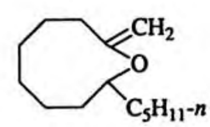
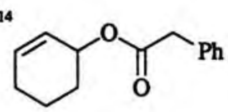
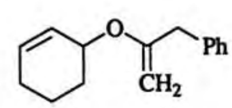
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (47)	137
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	63
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	138
	1. Tebbe, Tol 2. >C=O, THF, DMAP, -40 to 25°	 (—)	133
C_{14} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (96)	10

Table I. Methylenation of Esters (*Continued*)

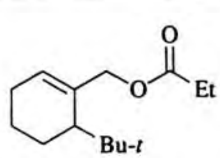
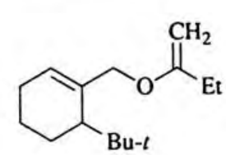
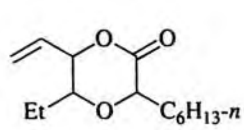
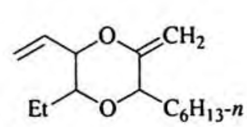
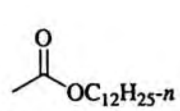
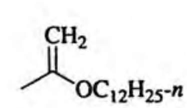
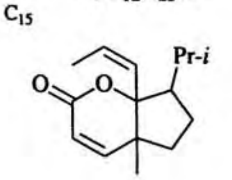
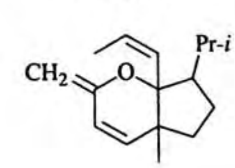
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (86)	60
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	101
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	" (65)	101
	Cp_2TiMe_2, Tol, >C=O, 65° 12-26 h (dark)	 (65)	131
C_{15} 	1. Tebbe, Tol, C_6H_6 2. >C=O, THF, Pyr 3. 180°, 24 h	 (91)	139

Table I. Methylenation of Esters (*Continued*)

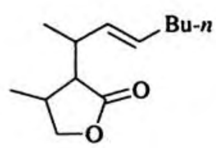
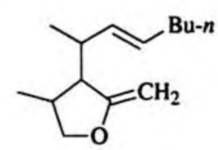
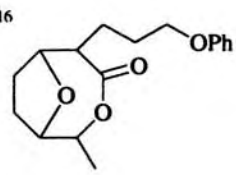
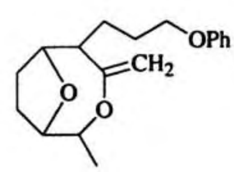
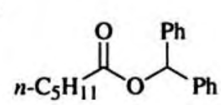
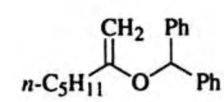
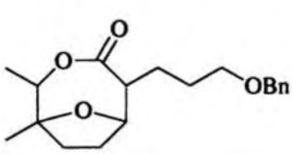
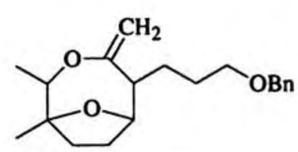
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	140
C_{16} 	1. Tebbe, Tol 2. >C=O, THF, Pyr, -45°	 (94)	123
C_{19} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (76)	137
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (94)	15

Table II. Methylenation of Ketones

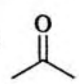
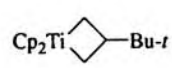
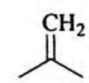
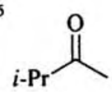
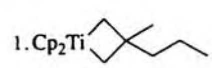
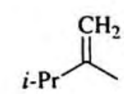
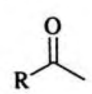
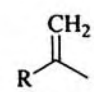
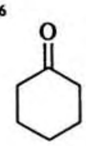
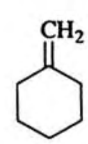
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 		 (90)	129
C_5 	1.  Et_2O, 0° 2. >C=O, rt, 30 min	 (>95)	24
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 R = n-C_5H_{11} (—) R = i-$C_3H_7(CH_2)_2$ (—) R = C_6H_{11} (—) R = $Me_2C{=}CH(CH_2)_2$ (—) R = n-C_6H_{13} (56) R = n-C_9H_{19} (—)	141
C_6 	1. Tebbe, Tol 2. >C=O, -15° to rt	 (65)	9
	1. $Cp_2Ti(Cl)CH{=}CHMe$, $HAl(Pr\text{-}i)_2$, Tol, -40° 2. >C=O	" (50)	30

Table II. Methylenation of Ketones (*Continued*)

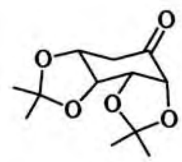
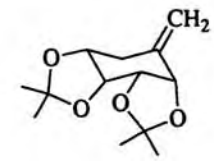
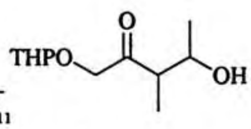
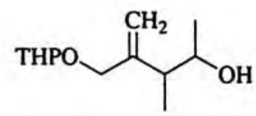
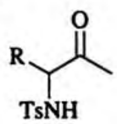
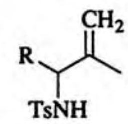
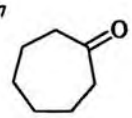
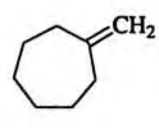
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (95)	142
C_6-C_{11} 	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	143
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	 R = i-Pr (—) R = i-Bu (—) R = Ph (—) R = Bn (—) R = $BnOCH_2$ (—)	144
C_7 	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 8 h	 (83)	11

Table II. Methylenation of Ketones (*Continued*)

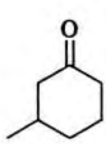
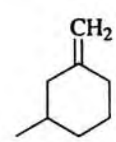
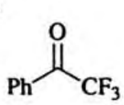
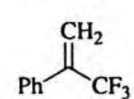
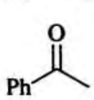
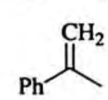
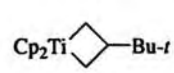
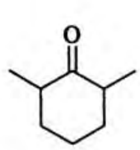
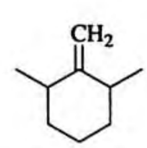
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	145
C_8 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (50)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (88-93)	12,23
		" (94)	129
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	" (90)	79
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (97)	23

Table II. Methylenation of Ketones (*Continued*)

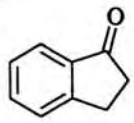
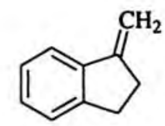
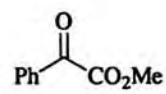
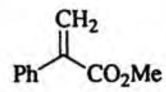
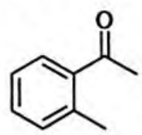
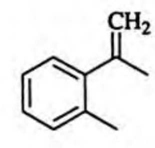
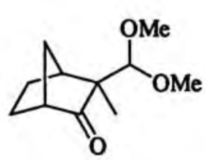
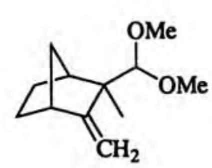
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Cp_2Ti  Et_2O, 0° 2. >C=O, rt, 30 min	" (>95)	24
C_9 	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	 (63)	79
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (31)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (98)	23
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (30)	91

Table II. Methylenation of Ketones (*Continued*)

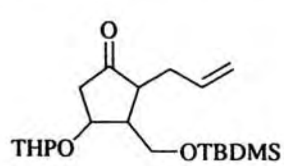
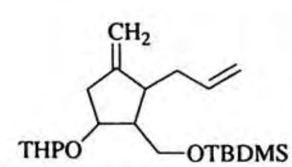
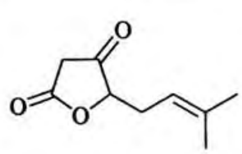
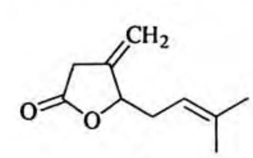
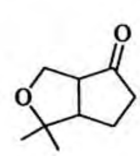
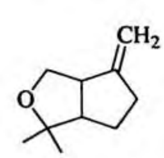
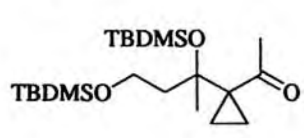
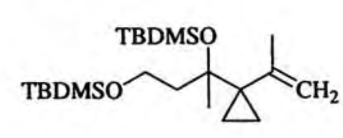
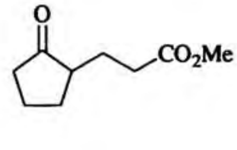
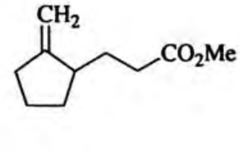
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	146
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (96)	147
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	148
	1. CH_2I_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	149
	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	 (60)	131

Table II. Methylenation of Ketones (*Continued*)

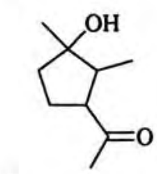
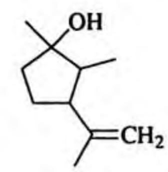
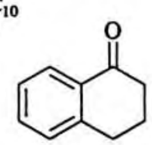
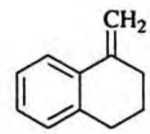
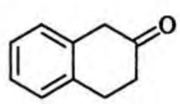
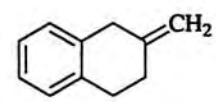
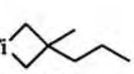
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (50)	97
C_{10} 	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15 min	 (88)	79
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	" (73)	12
	1. Tebbe, THF, -40° 2. >C=O, -40°, 30 min; rt, 8 h	 (84)	24
	1. Cp_2Ti  Et_2O, 0° 2. >C=O, rt, 30 min	" (70)	24

Table II. Methylenation of Ketones (*Continued*)

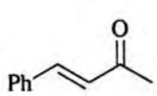
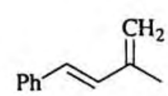
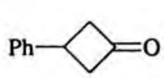
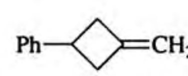
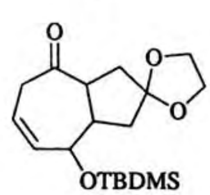
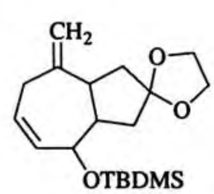
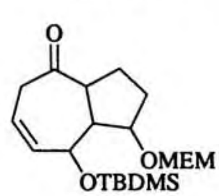
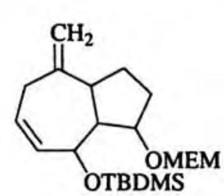
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	" (40)	12
	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	" (60)	131
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	 (78)	79
	$Cp_2TiCH_2ZnX_2$, Tol X = I, Cl	 (>80)	49
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (95)	150
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (99)	124

Table II. Methylenation of Ketones (*Continued*)

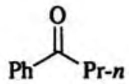
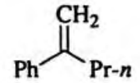
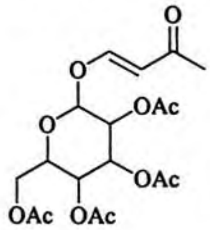
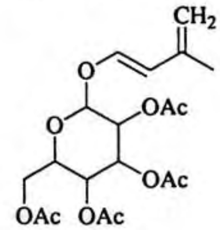
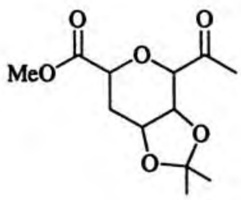
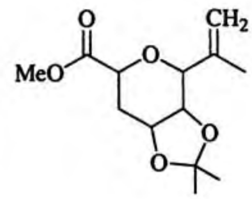
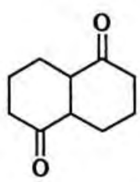
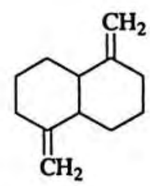
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (99)	12
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (45)	151
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	 (47)	152
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (56)	153

Table II. Methylenation of Ketones (*Continued*)

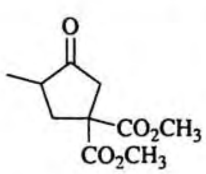
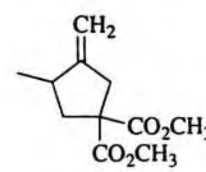
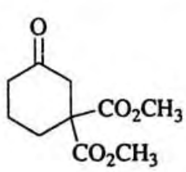
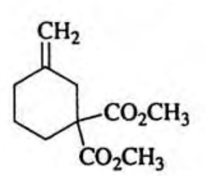
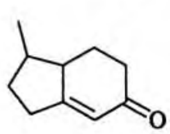
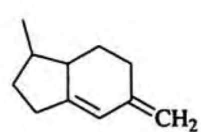
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	154
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	154
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (65)	155
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (71)	156
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (64-76)	156

Table II. Methylenation of Ketones (*Continued*)

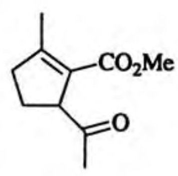
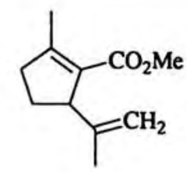
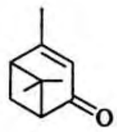
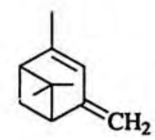
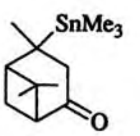
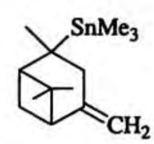
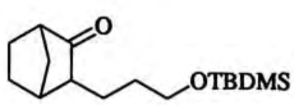
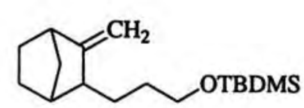
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (94)	93
	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	 (61)	131
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	157
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (93)	158

Table II. Methylenation of Ketones (*Continued*)

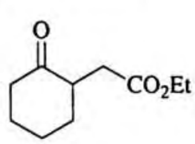
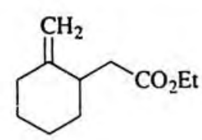
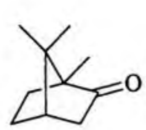
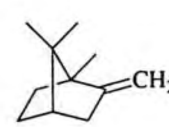
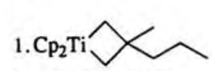
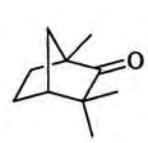
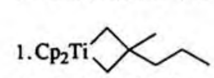
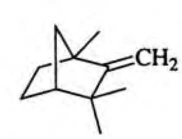
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (67)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (87)	24
	1.  Et_2O, 0° 2. >C=O, rt, 30 min	" (70)	24
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	" (73)	159
	1.  Et_2O, 0° 2. >C=O, rt, 30 min	 (20)	24
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	" (16)	24,12

Table II. Methylenation of Ketones (*Continued*)

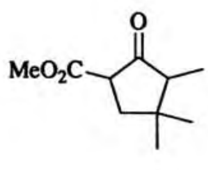
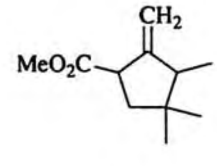
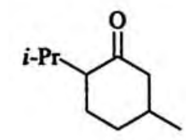
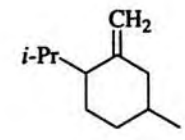
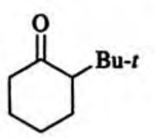
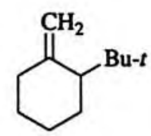
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 40 h	" (92)	11
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 1 h	" (64)	79
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 4 h	 (58)	80
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (89)	28
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (96)	23

Table II. Methylenation of Ketones (*Continued*)

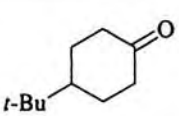
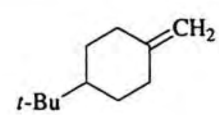
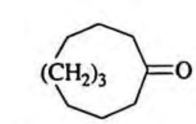
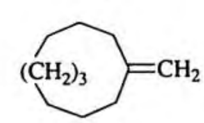
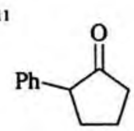
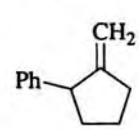
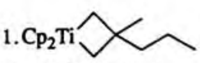
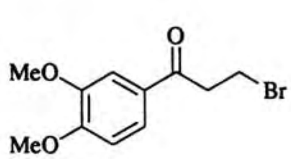
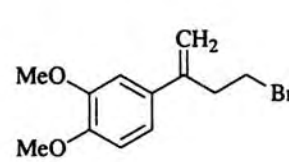
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn, CH_2Br_2, Cp_2TiCl_2 >C=O, THF, 3 h	 (17)	160
	1. Cp_2TiCl_2, $AlMe_3$, Tol 2. >C=O, -40°	" (75)	117
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (70)	161
C_{11} 	1. Tebbe, THF, -40° 2. >C=O, -40°, 30 min; rt, 1.5 h	 (89)	24
	1.  Et_2O, 0° 2. >C=O, rt, 30 min	" (98)	24
	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, -40°, 30 min; 0°, 1.5 h; rt, 1 h	 (93)	162

Table II. Methylenation of Ketones (*Continued*)

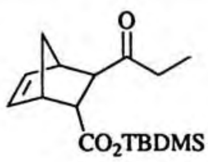
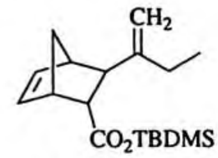
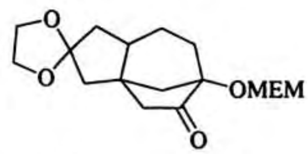
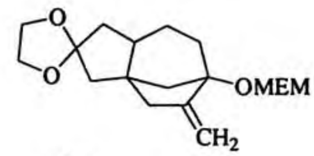
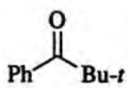
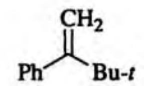
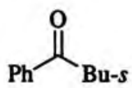
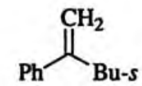
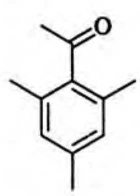
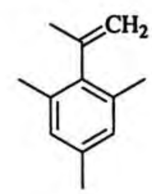
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (95)	163
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	164
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (96)	12, 23
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (98)	23
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (77)	23

Table II. Methylenation of Ketones (*Continued*)

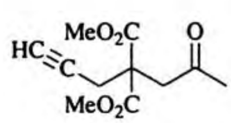
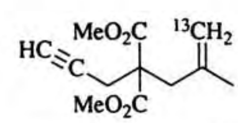
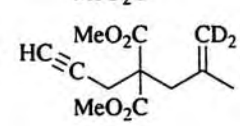
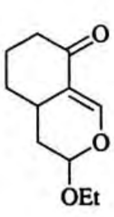
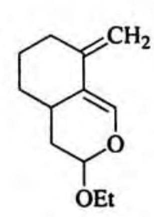
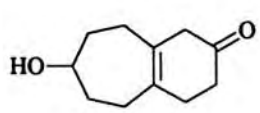
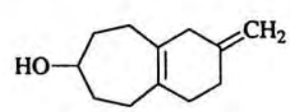
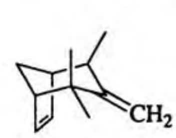
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, $^{13}CH_2Br_2$ 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	165
	1. Zn, THF, CD_2Br_2, 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	165
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (43)	166
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (61)	167
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (57-62)	156

Table II. Methylenation of Ketones (*Continued*)

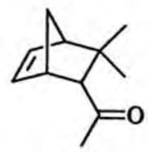
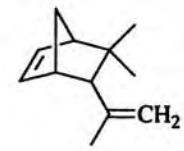
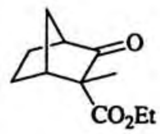
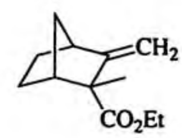
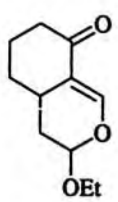
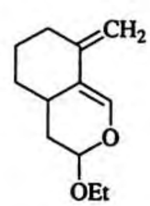
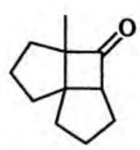
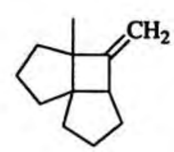
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (86-93)	168
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (40)	91
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (43)	166
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (55)	169

Table II. Methylenation of Ketones (*Continued*)

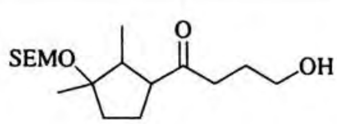
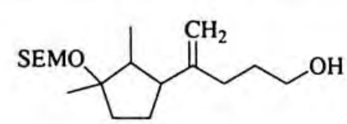
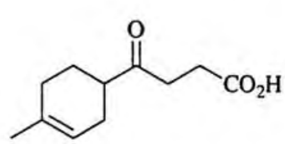
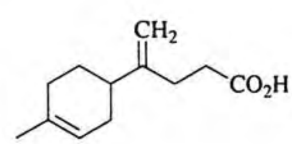
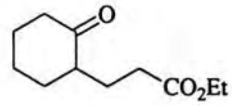
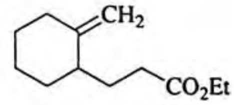
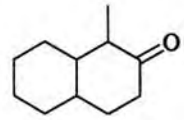
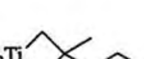
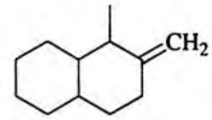
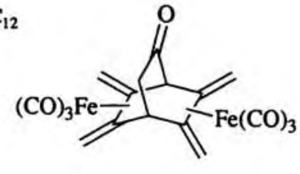
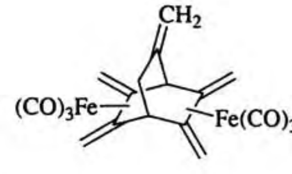
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (32)	170
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (66)	171
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	 (72)	79
	1. Cp_2Ti  Et_2O, 0° 2. >C=O, rt, 30 min	 (>95)	24
C_{12} 	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	 (58)	172

Table II. Methylenation of Ketones (*Continued*)

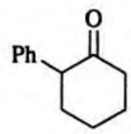
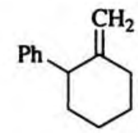
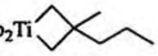
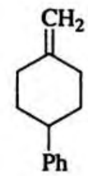
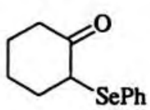
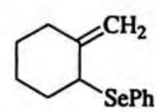
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, THF, -40° 2. >C=O, -40°, 30 min; rt, 1.5 h	 (93)	24
	1. Cp_2Ti Et_2O, 0° 2. >C=O, rt, 30 min	" (100)	24
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	" (88)	79
	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, -40°, 30 min; 0°, 1.5 h; rt, 1 h	 (82)	116
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	173

Table II. Methylenation of Ketones (*Continued*)

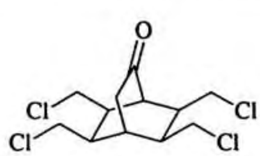
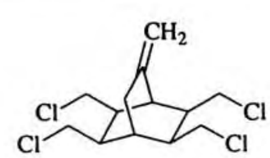
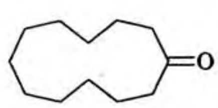
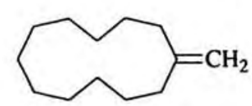
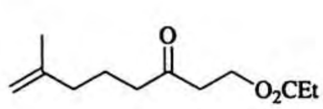
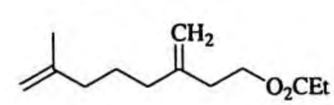
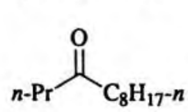
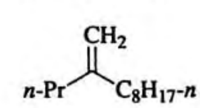
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (82)	174
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 20 min	 (90)	79
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	" (80)	11
	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	" (83)	131
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h		90
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (89)	11
	1. CH_2I_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	" (53)	51

Table II. Methylenation of Ketones (*Continued*)

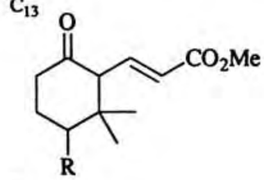
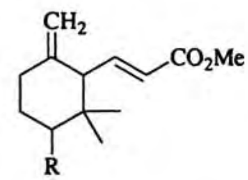
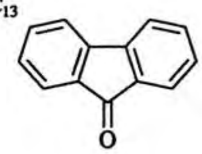
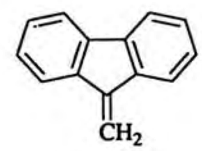
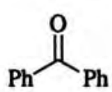
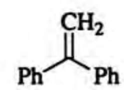
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2I_2, Zn, $TiCl_4$, THF 2. >C=O, CH_2Cl_2, $Ti(NEt_2)_4$ 3. 25°, 30 min	" (95)	51
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	" (86)	79
C_{12}- C_{13} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 R = H (100) R = Me (100)	175
C_{13} 	$Cl_2AlCH_2TiCl_3$, THF, heat 30 min	 (82)	52
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (97)	12, 23 9
	$Cl_2AlCH_2TiCl_3$, THF, heat 30 min	" (100)	52

Table II. Methylenation of Ketones (*Continued*)

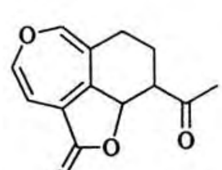
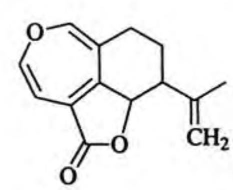
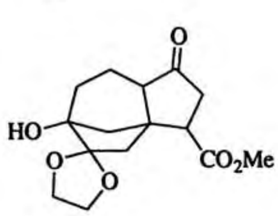
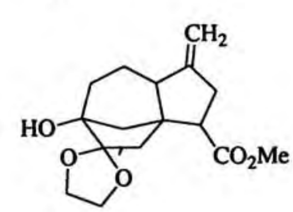
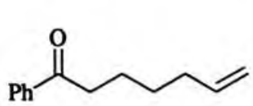
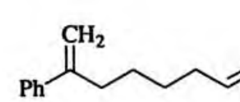
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cp_2TiCH_2ZnX_2$, Tol X = I, Cl	" (100)	49
	$(Cp_2TiBrCH_2)_2Mg$, THF 5°, 30 min	" (80)	29
	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	" (90)	131
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (98)	176
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	27, 98
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	121

Table II. Methylenation of Ketones (*Continued*)

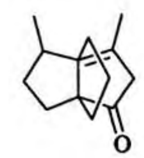
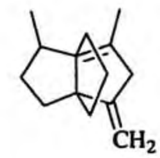
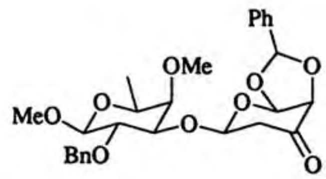
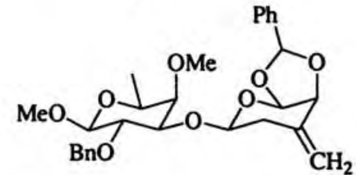
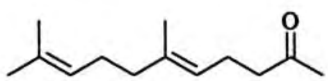
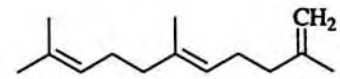
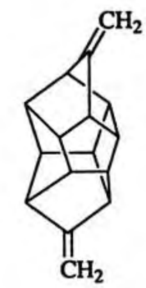
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (100)	177
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (92)	178
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (83)	11
C_{14} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	179

Table II. Methylenation of Ketones (*Continued*)

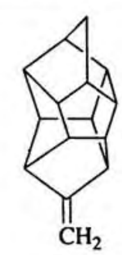
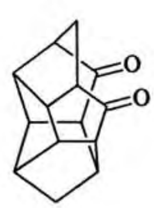
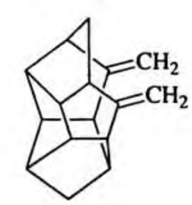
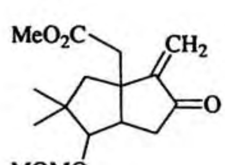
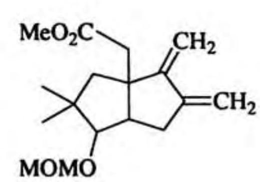
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	179
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	179
	1. Zn, THF, CH_2Br_2, 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 15 s	 (94)	180

Table II. Methylenation of Ketones (*Continued*)

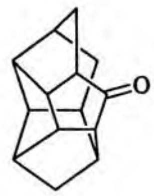
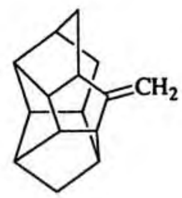
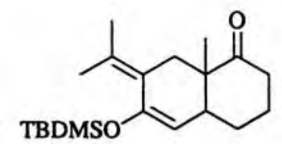
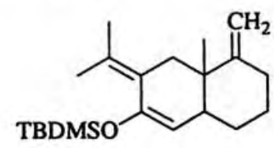
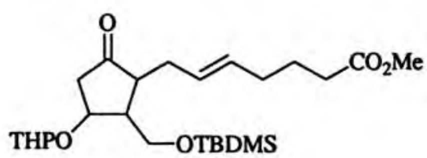
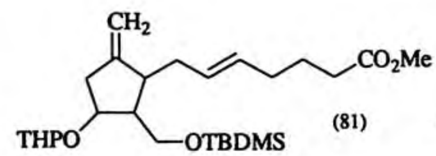
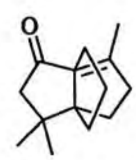
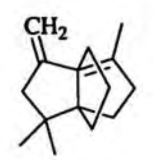
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	179
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (94)	82
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (81)	181
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min	 (52)	182

Table II. Methylenation of Ketones (*Continued*)

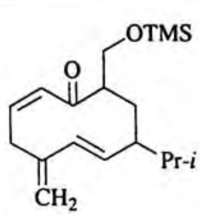
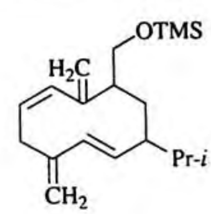
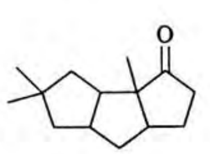
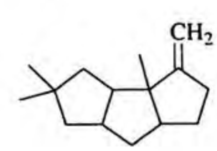
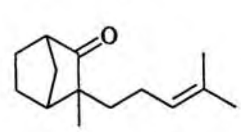
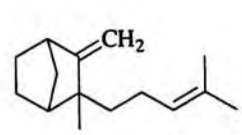
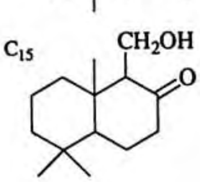
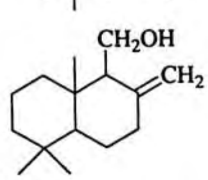
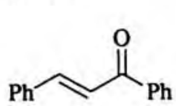
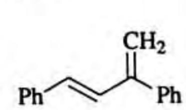
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (55)	183
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (100)	184
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (75)	158
C_{15} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (48)	185
	$Cp_2TiCH_2ZnX_2$, Tol X = I, Cl	 (>80)	49

Table II. Methylenation of Ketones (*Continued*)

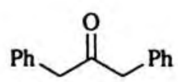
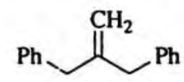
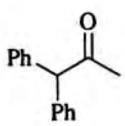
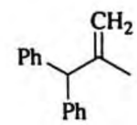
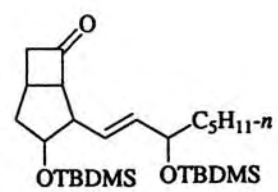
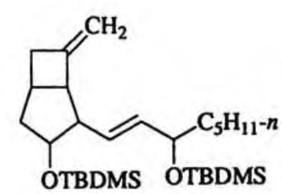
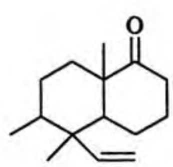
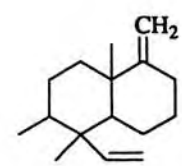
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15 min	 (79)	79
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (63)	23
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (70)	186
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	187

Table II. Methylenation of Ketones (*Continued*)

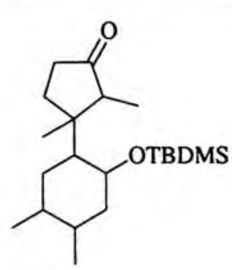
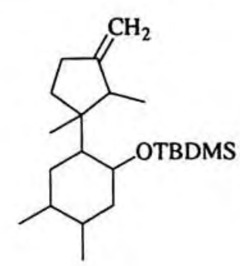
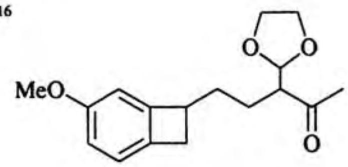
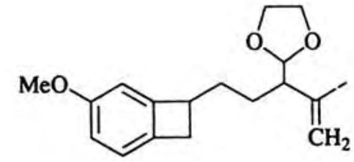
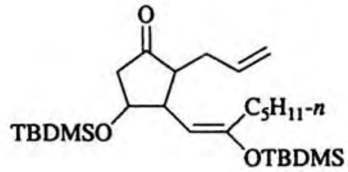
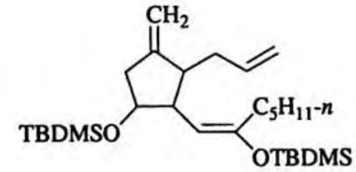
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (84)	78
C_{16} 	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (81)	188
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (90)	189

Table II. Methylenation of Ketones (*Continued*)

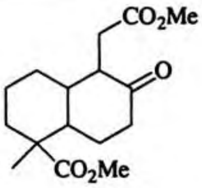
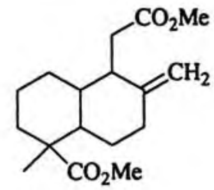
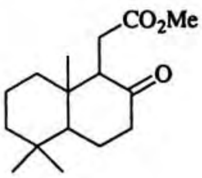
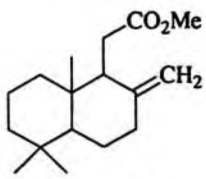
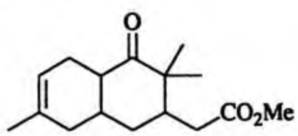
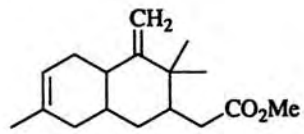
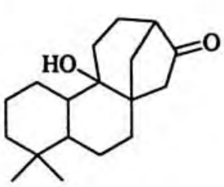
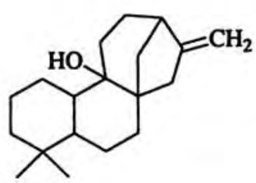
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h		(86)	92
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h		(72)	190
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h		(10-20)	191
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h		(85)	99

Table II. Methylenation of Ketones (*Continued*)

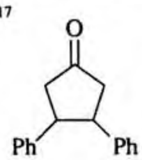
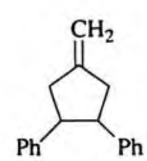
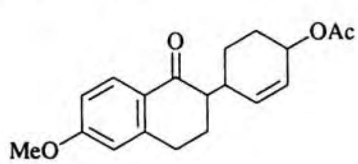
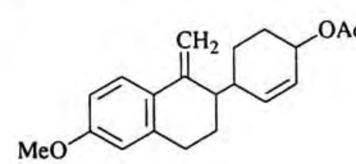
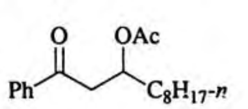
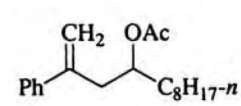
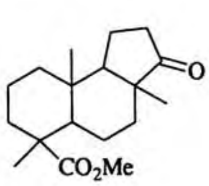
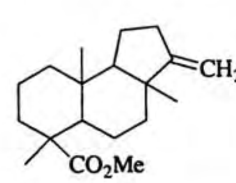
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17} 	1. Zn, CH_2I_2, THF, rt, 30 min 2. $TiCl_4$, 0°, 30 min 3. >C=O, THF		(92)	125
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h		(60)	81
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15-60 min		(73)	79
	1. $TiCl_4$, CH_2Cl_2, Zn, CH_2I_2, THF, 0°, 30 min 2. >C=O, THF, reflux 45 min		(55)	120

Table II. Methylenation of Ketones (*Continued*)

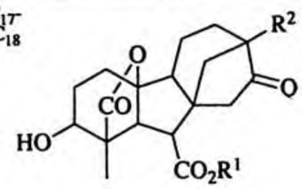
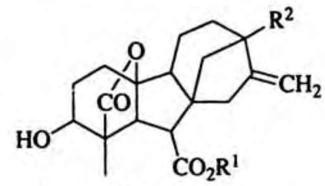
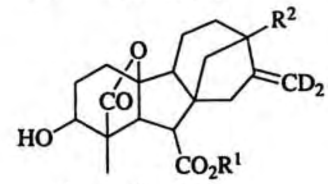
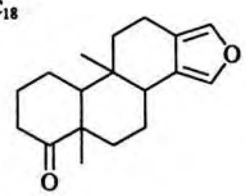
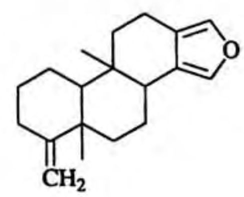
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}-C_{18} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 I R^1 / R^2 Me / H / I (93) H / H / I (80) Me / OH / I (38)	27
	1. Zn, THF, CD_2Br_2, 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 I R^1 / R^2 Me / H / I (—) H / H / I (—)	27
C_{18} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (62)	192

Table II. Methylenation of Ketones (*Continued*)

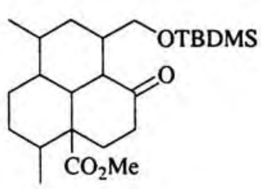
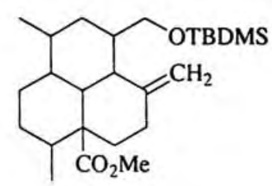
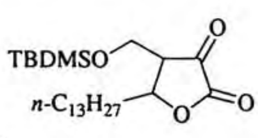
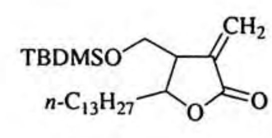
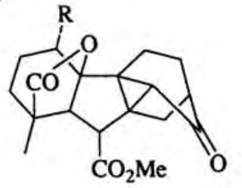
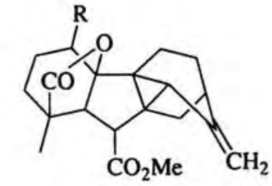
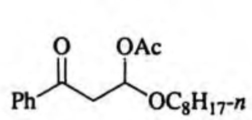
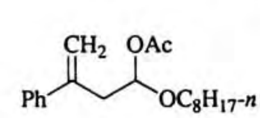
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (79)	193
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	143
C_{19} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 R = H (87) R = OH (83)	96
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 15 min	 (73)	79

Table II. Methylenation of Ketones (*Continued*)

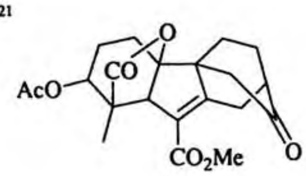
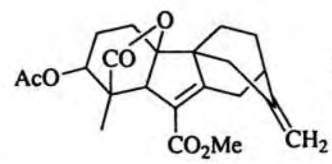
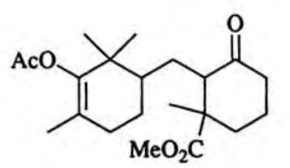
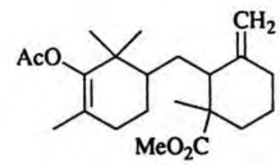
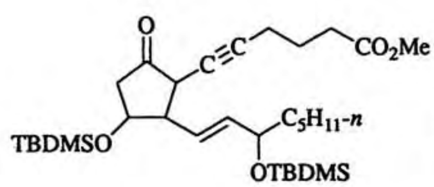
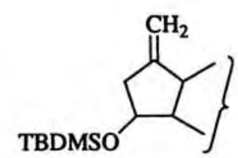
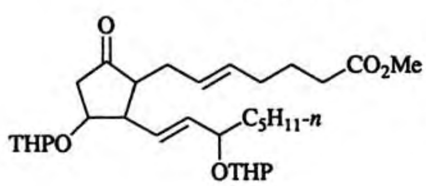
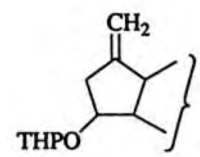
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21} 	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (79)	77
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (60)	194
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (97)	195
	1. Zn. THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (80)	196

Table II. Methylenation of Ketones (*Continued*)

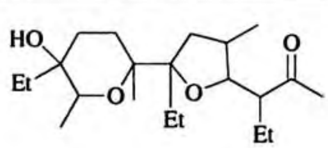
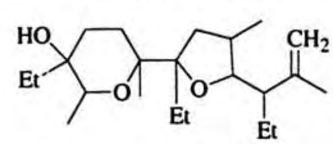
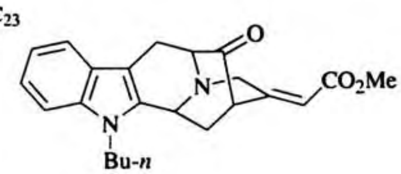
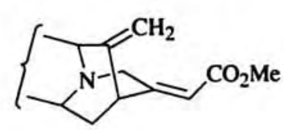
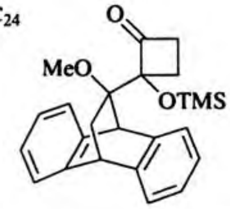
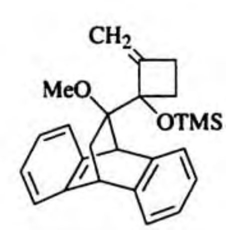
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (60-70)	15
C_{23} 	1. Cp_2TiCl_2, $AlMe_3$, Tol, 3 d 2. >C=O, THF, -40°, 30 min; 0°, 1.5 h; rt, 1 h	 (63)	197
C_{24} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (82)	198

Table III. Methylenation of Aldehydes

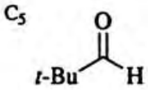
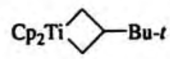
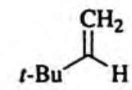
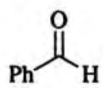
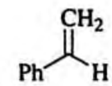
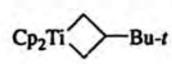
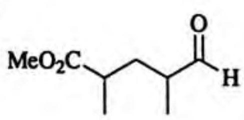
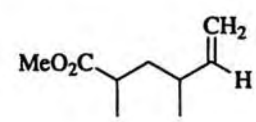
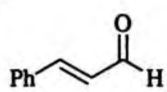
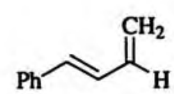
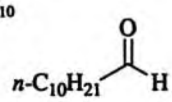
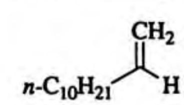
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 		 (100)	129
C_7 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	9
		" (92)	129
C_8 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (40)	95
C_9 	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	 (52)	79
C_{10} 	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	 (43)	131

Table III. Methylenation of Aldehydes (*Continued*)

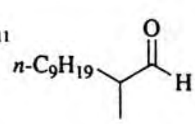
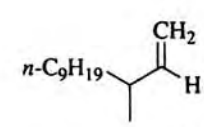
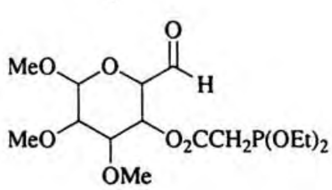
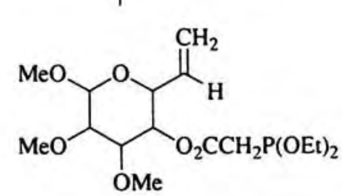
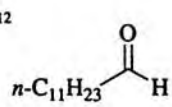
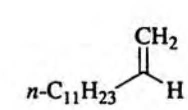
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	Cp_2TiMe_2, Tol, >C=O, 65°, 12-26 h (dark)	 (62)	131
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	199
C_{12} 	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 0°, 4 h	 (55)	11
	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	" (10)	51
	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	" (74)	27
	1. CH_2I_2, Zn, THF, 30 min 2. $TiCl_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 30 min	" (78)	51, 79

Table III. Methylenation of Aldehydes (*Continued*)

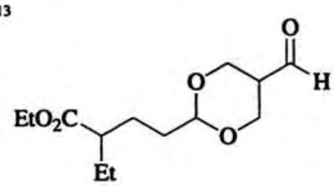
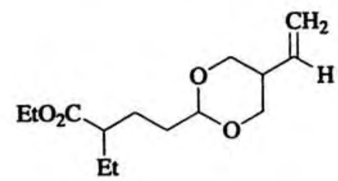
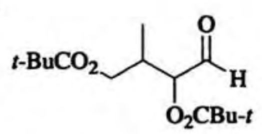
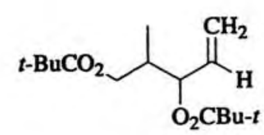
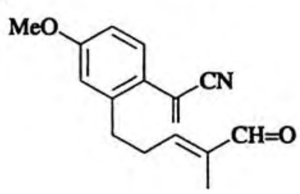
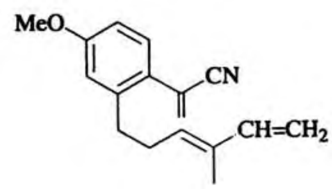
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. CH_2I_2, Zn, THF, 30 min 2. $Ti(OPr\text{-}i)_4$, CH_2Cl_2, 0°; 25°, 30 min 3. >C=O, THF, 25°, 5 h	" (86)	51
C_{13} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (35)	94
C_{15} 	1. Tebbe, Tol-C_6H_6 2. >C=O, THF, Tol, Pyr, -40°; 3. -40°, 30 min; rt, 90 min	 (48)	89
C_{16} 	1. CH_2Br_2, Zn, THF 2. $TiCl_4$, CH_2Cl_2, 25°, 15 min 3. >C=O, THF, 25°, 12 h	 (—)	62

Table III. Methylenation of Aldehydes (*Continued*)

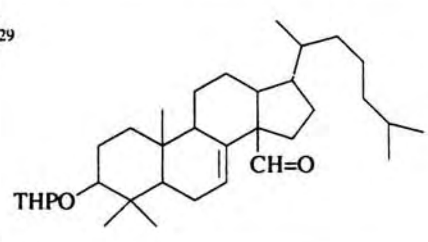
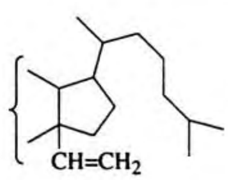
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{29} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1.5 h	 (—)	200

Table IV. Methylenation of Amides

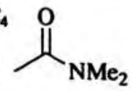
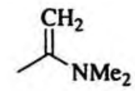
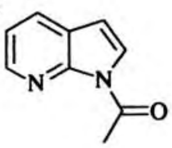
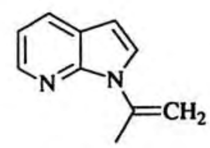
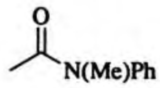
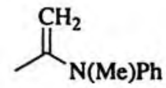
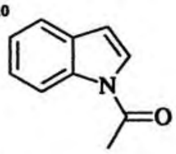
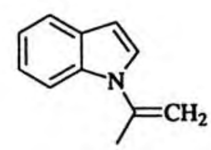
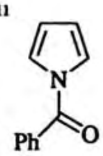
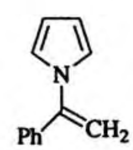
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (—)	12
C_9 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (56)	201
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (97)	12
C_{10} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (50)	201
C_{11} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (74)	201

Table IV. Methylenation of Amides (*Continued*)

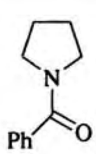
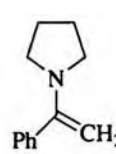
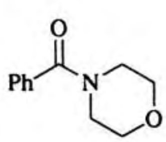
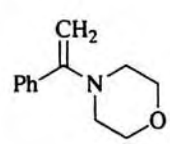
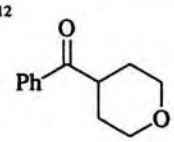
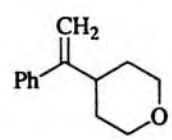
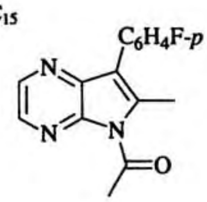
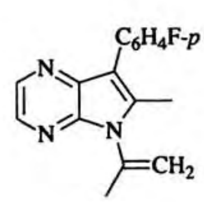
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (80)	12
	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (67)	12
C_{12} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (76)	12
C_{15} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (51	201

Table IV. Methylenation of Amides (*Continued*)

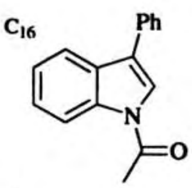
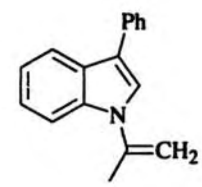
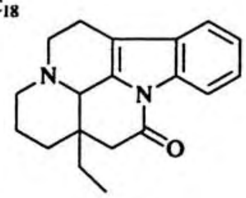
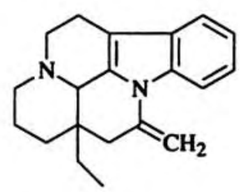
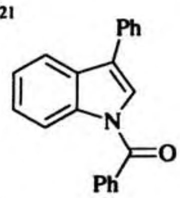
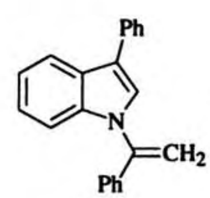
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (55)	201
C_{18} 	1. Zn, THF, CH_2Br_2 2. $TiCl_4$, -40°; 5°, 3 d 3. >C=O, CH_2Cl_2, 20°, 1 d	 (85)	17
C_{21} 	1. Tebbe, Tol 2. >C=O, THF, 0° 3. 0° to rt, 30 min	 (68)	201

Table V. Alkylidenation of Esters

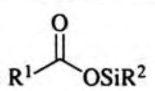
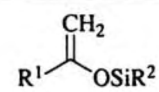
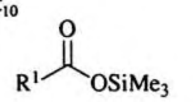
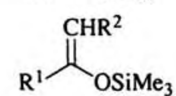
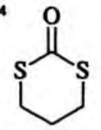
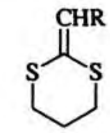
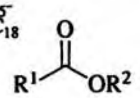
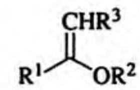
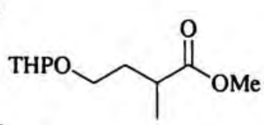
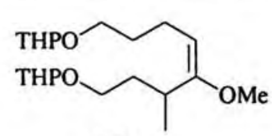
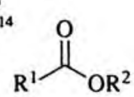
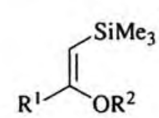
Reactant	Conditions	Product(s) and Yield(s) (%)				Refs.
C_2 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^3CHBr_2, THF, 25°, 1.5-2 h					19
		R^1	R^2	R^3		
		Me	Me_2Bu-*t*	Bn	(78)	
		Me	$(i\text{-}Pr)_3$	Bn	(91)	
C_2-C_{10} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^2CHBr_2, THF, 25°, 1.5-2 h					19
		R^1	R^2			
		Me	Bn	(79)		
		n-C_5H_{11}	Bn	(76)		
		Ph	Me	(90)		
		Ph	*n*-Bu	(84)		
		Ph	Bn	(87)		
		Ph	C_6H_{11}	(74)		
		C_6H_{11}	Me	(80)		
		C_6H_{11}	*n*-Bu	(78)		
		C_6H_{11}	Bn	(84)		
		PhCH=CH	Me	(65)		
		PhCH=CH	*n*-Bu	(79)		
		PhCH=CH	Bn	(79)		
		$PhCH_2CH_2$	*n*-Bu	(80)		
		n-C_9H_{19}	Me	(77)		
		n-C_9H_{19}	*n*-Bu	(80)		
		n-C_9H_{19}	Bn	(66)		
		n-C_9H_{19}	C_6H_{11}	(68)		

Table V. Alkylidenation of Esters (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, $RCHBr_2$, THF, 25°, 0.3-1.3 h		18
C_5-C_{18} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^3CHBr_2, THF, 25°, 2-3 h		14

R^1	R^2	R^3	
i-Pr	Me	*n*-C_5H_{11}	(89)
n-Bu	Me	*i*-Bu	(95)
n-Bu	Me	C_6H_{11}	(69)
i-Bu	Me	*n*-C_5H_{11}	(88)
n-Bu	Me	*n*-C_5H_{11}	(96)
MeCH=CH	Et	*c*-C_5H_{11}	(90)
n-Bu	CH_2=$CHCH_2$	*c*-C_5H_{11}	(52)
Ph	Me	Me	(86)
Ph	Me	*n*-C_5H_{11}	(89)
Ph	Me	*i*-Bu	(79)
Ph	Me	C_6H_{11}	(61)
Ph	*i*-Pr	Me	(88)
Me	*n*-C_8H_{17}	Me	(68)
Ph	*t*-Bu	Me	(81)
n-Pr	*n*-PrCH=$CHCH_2$	*n*-C_5H_{11}	(85)
CH_2=CHC_8H_{17}-*n*	Me	Me	(53)
Ph	Ph	Me	(76)
Ph	Ph	H	(16)
n-$C_{11}H_{23}$	Me	Me	(75)
n-$C_8H_{17}CH$=CHC_7H_{15}-*n*	Me	Me	(70)

Table V. Alkylidenation of Esters (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_3CHBr_2$, rt, 4 h	 (83)	50
C_6-C_{14} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 15 min 3. Zn, 25°, 30 min 4. >C=O, $Me_3SiCHBr_2$, CH_2Cl_2, 25°, 3-5 h		26

R^1	R^2	
MeCH=CH	Et	(81)
Ph	Me	(84)
C_6H_{11}	Me	(90)
n-Pr	*n*-PrCH=$CHCH_2$	(92)
n-$C_{11}H_{23}$	Me	(92)
n-C_9H_{19}	CH_2=$CHCH_2$	(78)
n-C_8H_{17}	$(MeO)_2CH(CH_2)_2$	(94)

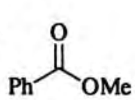
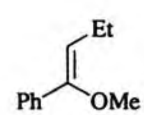
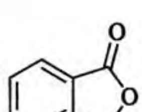
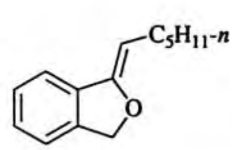
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	1. $Cp_2TiClCH$=CHMe, $HAl(Bu$-$i)_2$, Tol, -40° to rt, 30 min 2. >C=O	 (—)	30
	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, *n*-$C_5H_{11}CHBr_2$, THF, 25°, 2 h	 (58)	14

Table V. Alkylidenation of Esters (*Continued*)

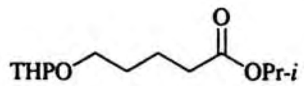
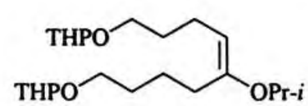
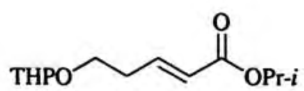
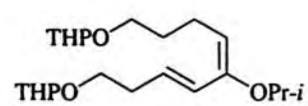
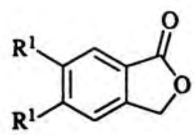
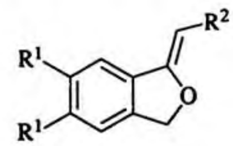
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_3CHBr_2$, rt, 4 h		(88)	50
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_3CHBr_2$, rt, 2.5 h		(86)	50
	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^2CHBr_2, THF, 25°, 2 h	 R^1 / R^2 H / Ph (—) H / Bn (—) H / CH_2=$CHCH_2$ (—) OMe / Ph (—) OMe / CH_2=$CHCH_2$ (—) OMe / CH_2=$CH(CH_2)_2$ (—) H / CH_2=$CH(CH_2)_3$ (—)		16

Table V. Alkylidenation of Esters (*Continued*)

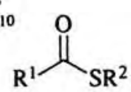
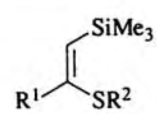
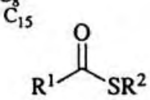
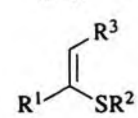
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8-C_{10} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 15 min 3. Zn, 25°, 30 min 4. >C=O, $Me_3SiCHBr_2$, CH_2Cl_2, 25°, 2-5 h	 R^1 / R^2 Ph / Me (64) n-C_8H_{17} / Me (80) C_6H_{11} / Me (88)	26
C_8-C_{15} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^3CHBr_2, THF, 25°, 0.5-5 h	 R^1 / R^2 / R^3 Ph / Me / Me (77) Ph / Me / n-Bu (75) Ph / Me / Bn (80) C_6H_{11} / Me / Me (88) C_6H_{11} / Me / Bn (95) C_6H_{11} / Me / C_6H_{11} (97) n-C_8H_{17} / Me / Me (94) n-C_8H_{17} / Me / C_6H_{11} (95) n-C_8H_{17} / Me / Bn (87) Ph / Ph / Me (56) C_6H_{11} / Ph / Me (79) n-C_8H_{17} / Ph / Me (71)	18

Table V. Alkylidenation of Esters (*Continued*)

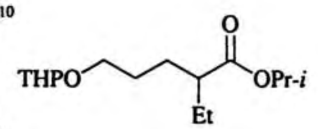
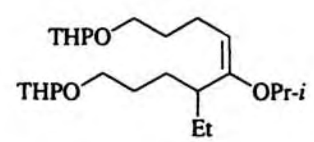
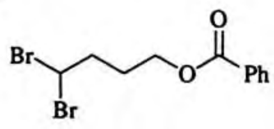
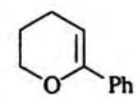
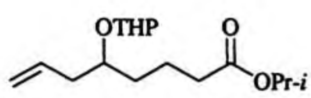
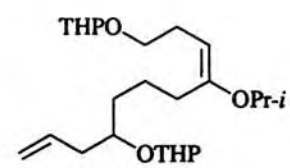
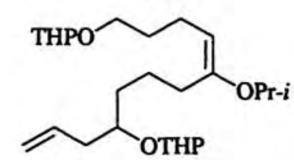
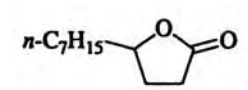
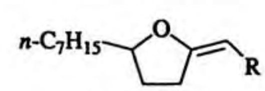
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10} 	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_3CHBr_2$, rt, 4 h		(89)	50
C_{11} 	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. rt, 24 h		(15)	50
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_2CHBr_2$, rt, 20 h		(61)	50
	1. $TiCl_4$, THF, 0° 2. TMEDA, rt, 10 min 3. Zn, rt, 30 min 4. >C=O, $THPO(CH_2)_3CHBr_2$, rt, 20 h		(92)	50
	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, $RCHBr_2$, THF, 25°, 1.5-2 h	 R = Me (41) R = n-C_5H_{11} (21)		14

Table V. Alkylidenation of Esters (*Continued*)

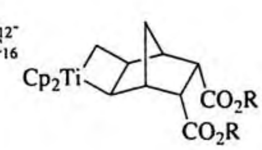
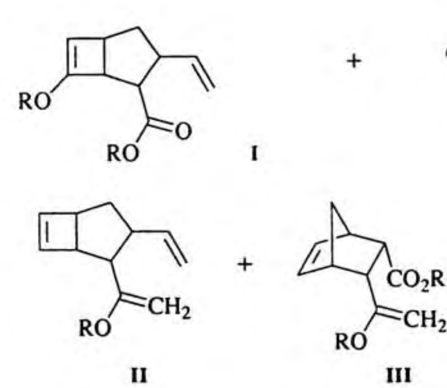
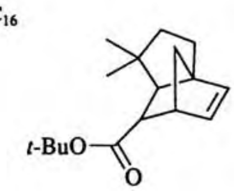
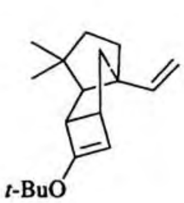
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}-C_{16} 	70°, 11 h	 R = Me, I (7) + II (12) + III (22) R = Et, I (22) + II (7) + III (11) R = i-Pr, I (39) + II (—) + III (—)		66
C_{16} 	1. Tebbe, THF, DMAP 2. 90°		(81)	65

Table V. Alkylidenation of Esters (*Continued*)

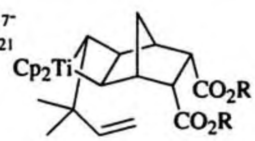
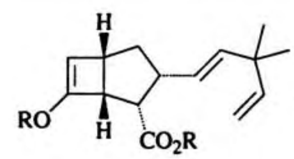
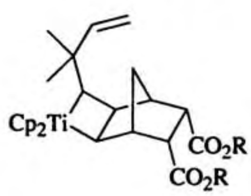
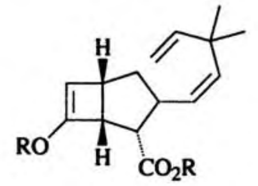
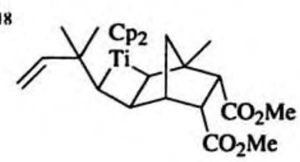
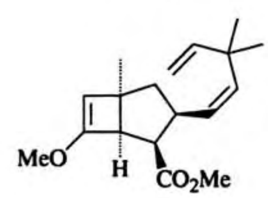
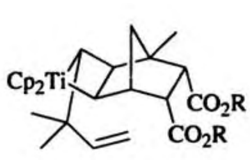
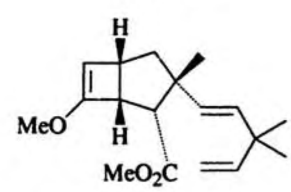
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}-C_{21} 	55°, 15 h	 R = Me (46) R = *i*-Pr (57)	66
	55°, 15 h	 R = Me (15) R = *i*-Pr (23)	66
C_{18} 	65°, 12 h	 (22)	66
	65°, 12 h	 (44)	66

Table VI. Alkylidenation of Ketones and Aldehydes

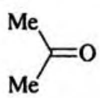
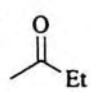
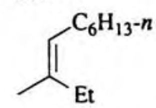
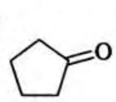
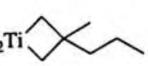
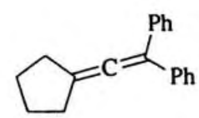
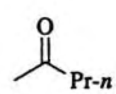
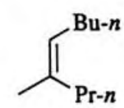
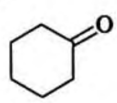
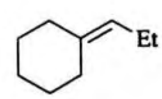
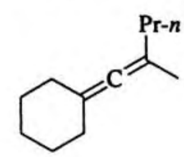
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	n-$C_5H_{11}CH=CHAl(Bu$-$i)_2$, Cp_2TiCl_2	$Me_2C=C=CHC_6H_{13}$ (64)	84
C_4 	n-$C_5H_{11}CH=CHAl(Bu$-$i)_2$, Cp_2TiCl_2	 (62)	84
C_5 	1. Cp_2Ti  , C_6H_6, $Ph_2C=C=CH_2$, 15 min 2. >C=O, rt, 12 h	 (72)	87
	1. n-$PrCH=CHAl(Bu$-$i)_2$, Cp_2TiCl_2, CH_2Cl_2, 0°, 1 h 2. >C=O, -50°	 (70)	84
C_6 	1. $Cp_2TiClCH=CHMe$, $HAl(Bu$-$i)_2$, Tol, -40° to rt, 30 min 2. >C=O	 (50)	30
	n-$PrCMe=C(AlMe_2)TiCp_2Cl$	 (83)	85

Table VI. Alkylidenation of Ketones and Aldehydes (*Continued*)

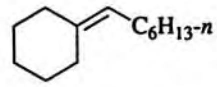
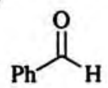
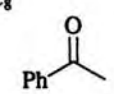
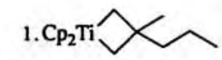
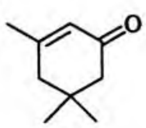
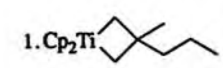
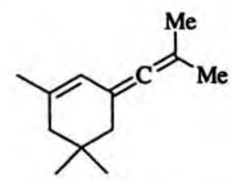
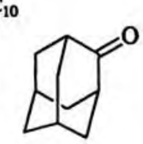
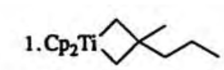
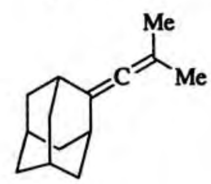
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	n-$C_5H_{11}CH$=CHAl(Bu-i)$_2$, Cp_2TiCl_2	 (61)	84
C_7 	n-PrCMe=C($AlMe_2$)$TiCp_2Cl$	Ph(H)C=C=C(Me)Pr-n (67)	85
C_8 	1. , C_6H_6, Me_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	Ph(Me)C=C=C(Me)Me (56)	87
C_9 	1. , C_6H_6, Me_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	 (55)	87
C_{10} 	1. , C_6H_6, Me_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	 (75)	87

Table VI. Alkylidenation of Ketones and Aldehydes (*Continued*)

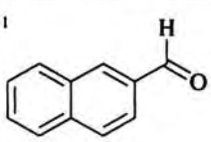
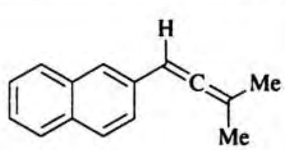
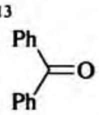
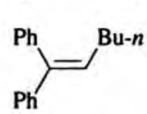
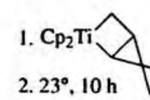
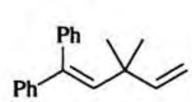
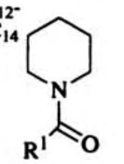
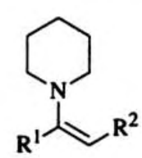
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	1. , C_6H_6, Me_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	 (53)	87
C_{13} 	1. , C_6H_6, CH_2=C=CH_2, 15 min 2. >C=O, rt, 12 h	Ph_2C=C=CH_2 (58)	87
	1. , C_6H_6, Me_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	Ph_2C=C=CMe_2 (80)	87
	1. n-PrCH=CHAl(Bu-i)$_2$, Cp_2TiCl_2, CH_2Cl_2, 0°, 1 h 2. >C=O, -50°	 (61)	84
	1.  Tol, >C=O, 0° 2. 23°, 10 h	 (83)	44
	1. , C_6H_6, Ph_2C=C=CH_2, 15 min 2. >C=O, rt, 12 h	Ph_2C=C=CPh_2 (56)	87

Table VII. Alkylidenation of Amides

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}-C_{14} 	1. $TiCl_4$, CH_2Cl_2, THF, 0° 2. TMEDA, 25°, 10 min 3. Zn, 25°, 30 min 4. >C=O, R^2CHBr_2, THF, 25°, 3-18 h		18

R^1	R^2	
Ph	Me	(70)
Ph	*n*-Bu	(80)
Ph	Bn	(87)
C_6H_{11}	Me	(82)
n-C_8H_{17}	Me	(—)

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The Baeyer–Villiger Oxidation of Ketones and Aldehydes

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1. Introduction

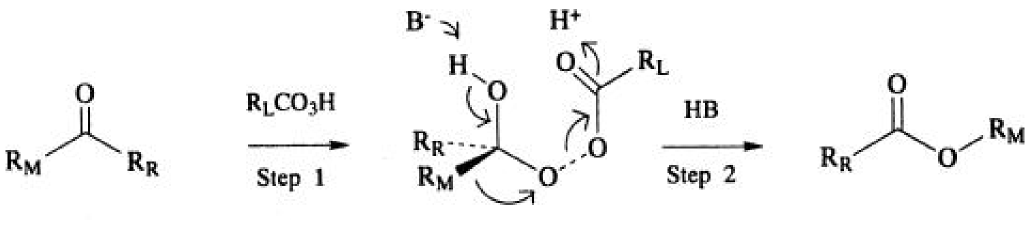
The oxidative conversion of alicyclic ketones into lactones with permonosulfuric acid was discovered by Baeyer and Villiger in 1899, (1) and in their honor the general process by which ketones are converted into esters or lactones is now known as the Baeyer–Villiger reaction. The literature on this synthetically useful process has been reviewed comprehensively through 1953 in Volume 9 of *Organic Reactions*, (2) and less comprehensive reviews of the reaction have appeared since then. 3–10g More recent investigations have led to the development of new synthetic reagents, to improvements in experimental reaction conditions, and to a better understanding of regiochemical and stereochemical aspects of the reaction. Baeyer–Villiger reactions now often can be carried out with functional group chemoselectivity and regiochemical control. Although the recent removal from commerce of 90% hydrogen peroxide and reagents based upon this oxidant are a setback to Baeyer–Villiger reaction methodology, alternative reagents, catalysts, and methods described in this review are available to fill the gaps.

The definition of the Baeyer–Villiger reaction is somewhat fuzzy, and can be considered to include both ketones and aldehydes. In addition to the traditional use of organic and inorganic peracids as oxidants, examples of oxygen insertion reactions using hydrogen peroxide, alkyl peroxides, and several metal ion oxidants are considered to fall within the scope of this chapter and are included in the tabular survey.

2. Mechanism

2.1. The Criegee Mechanism

The two-step ionic mechanism for the Baeyer–Villiger oxidation outlined by Criegee (11) continues to be generally accepted. Evidence for this mechanism obtained prior to 1953 is discussed in the previous review of this reaction. (2) As shown in Eq. 1, addition of peracid in step 1 to the ketone carbonyl provides a tetrahedral intermediate **1**. This step can be catalyzed by acid or base. (12) In step 2 the group R_M migrates with retention of configuration to oxygen as the O - O bond breaks and releases the leaving group to provide product ester or lactone.



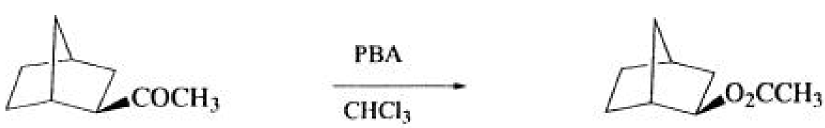
(1)

1

The two-step ionic mechanism for the Baeyer-Villiger reaction.

2.2. Nature of the Migration Step

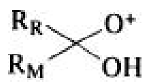
Evidence in support of a concerted migration step 2 includes stereochemical and isotopic labeling results, kinetic studies, and theoretical calculations. The migrating group is not free, since oxidation of (n)-*exo*-norbornyl ketone **2** with perbenzoic acid (PBA) in chloroform provides *exo*-acetate **3** with 94–100% retention of optical purity. Failure to observe racemization or *exo/endo* isomerization indicates the migrating group moves with its electrons. (13)



(–) 2

(–) 94-100% retention (86%) 3

The leaving group does not leave intermediate 1 prior to migration. Oxidation of ^{18}O-carbonyl labeled benzophenone, *p*-methoxybenzophenone, and fluorenone with 40% peracetic acid/acetic acid/chloroform provides ester with the isotopic label in the carbonyl oxygen. This excludes a mechanism with equivalent oxygens such as an intermediate oxonium ion species **4** in which hydrogen exchange might occur. (14) Also, in the oxidation of cyclohexyl phenyl ketone in ethylene chloride at 30° there is a greater regioselectivity for cyclohexyl migration with peracetic acid than trifluoroperacetic acid (TFPAA). This result is inconsistent with a common intermediate, such as an oxonium ion, and suggests that migration occurs while the carboxylic acid residue is leaving the Criegee intermediate. (15)



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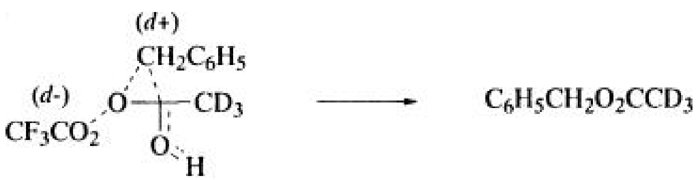
Isotope effects support a migration in concert with departure of the leaving group. A secondary beta deuterium–isotope effect k_H/k_D = 1.052/D is calculated for the TFPAA oxidation of phenyl-2-propanone. The positive value indicates a partial carbonyl bond adjacent to the nonmigrating methyl group in the transition state **5** for shifting of the benzyl group. (16) Significant ^{14}C isotope effects when X = CN, Cl, H, CH_3 (k_{12}/k_{14} = 1.084 to 1.032) are found for *m*-chloroperbenzoic acid



5

(MCPBA) oxidation of *para*-X-substituted acetophenones-1-^{14}C. The isotope effects are expected for rate-determining aryl migration from **1** in step 2, but rule out both formation of the Criegee intermediate and breaking of the O -O bond without concomitant rearrangement as rate-determining steps. (17)

Theoretical models, which trace the timing of the migration from carbon to oxygen during step 2 of the Baeyer–Villiger rearrangement, are consistent with the experimental results. MINDO-3 calculations rule out rate-determining migration to a cationic oxygen for reaction of performic acid with cyclobutanone. (18) Nonempirical SCF-MO and CNDO/2 treatments, which trace methyl migration in a model reaction, indicate little reorganization in the migrating methyl group and considerable carbonyl formation. (19)

2.3. Rate-Determining Migration

Most evidence indicates that the concerted migration step 2 is rate determining. (16, 17, 20, 21) Aryl substituents do not affect the Baeyer–Villiger reaction of aryl ketones in the same way as reactions known to proceed by rate-determining addition. For example, rates of simple carbonyl addition reactions such as oximation and semicarbazone formation can be correlated by a linear free energy relationship, (22) but a linear relationship does not exist between the free energies of activation for the Baeyer–Villiger reaction of dialkyl, cycloalkyl, and methyl phenyl ketones and the free energies of activation for oximation of the same ketones. This suggests that decomposition of the Criegee intermediate is rate determining. (23)

Baeyer–Villiger reaction rates generally are not those expected for rate-determining carbonyl addition. Cyclohexanone reacts 200 times slower with peracetic acid than with TFPAA using trifluoroacetic anhydride catalyst in ethylene chloride at 30°. Since the weakly nucleophilic TFPAA should be less reactive than peracetic acid toward carbonyl addition, the observed rate difference strongly favors rate-determining decomposition of the Criegee intermediate. (15)

Electron withdrawal on the leaving group facilitates the rate-determining migration step as indicated by the small positive values [$\rho = 0.2–0.4$ (σ)] noted for the oxidation of benzaldehyde with substituted perbenzoic acids at $pH < 9$. (12) Acid catalysis also facilitates loss of the leaving group at low pH. (12, 23-27)

Electron-donating groups on the migrating group facilitate the rearrangement. Rate data for TFPAA oxidation of *p*-substituted acetophenones in acetonitrile or ethylene chloride (23) and peroxomonophosphoric acid (PMPA) in acetonitrile (28) plotted versus substituent values give similar negative ρ values ($\rho = –1.45$, –1.10, and –2.55). For Hammett plots of the kinetic data for MCPBA oxidation of the same substrates in chloroform, a better linear fit is observed with ($\rho = –1.36$). (17) Peroxomonosulfate (PMSA) oxidations of substituted aryl aldehydes also show a negative value ($\rho = –1.70$), (26) and negative ρ values –5.7 and –3.8 (σ^{+})] were revealed for aryl migration of substituted benzaldehydes in acidic and neutral media. (12) Carbonyl addition reactions normally give moderate positive ρ values; (23) the negative ρ values are consistent with an activated complex which is electron deficient on the migrating group during the rate-determining step 2.

Caution must be exercised in using reaction ρ values to interpret mechanisms, since the equilibrium constant for formation of the Criegee intermediate prior to the rate-determining migration step affects the observed rate data. Hammett results cannot be explained straightforwardly at moderate acidity, but stronger peracids cause fast equilibrium formation of the Criegee intermediate and give clearer kinetics. (29)

2.4. Rate-Determining Addition

Rate-determining addition (Step 1 of Eq. 1) has been postulated for aryl aldehydes and ketones substituted with strongly electron-donating groups. For MCPBA oxidation of *p*-methoxyacetophenone a negligible carbon isotope effect $k_{12}/k_{14} = 0.998$ was observed. If there is no equilibrium isotope effect for addition of peracid to the ketone carbonyl, (16) the absence of an isotope effect is consistent with rate-controlling addition of peracid to the ketone carbonyl. (17)

Evidence suggests rate-determining addition to carbonyl for the perbenzoic acid oxidation of *o*- and *p*-hydroxybenzaldehydes in aqueous ethanol. For *p*-methoxybenzaldehyde migration appears to be rate determining above pH 5, whereas the apparent rate below pH 5 is controlled by both addition and migration. (12) In benzene and ethanol solvents migration appears to be rate determining. (29)

A rate-determining addition step 1 (Eq. 1) has been suggested for acid-catalyzed reactions of peroxymonophosphoric acid in aqueous acetic acid with several cyclopentanones and cyclohexanones on the basis of reactivity, activation energy and entropy values, solvent, and catalyst effects. (25) Rate-determining addition occurs in the oxidation of biacetyl and benzil with peroxomonosulfuric acid and peroxomonophosphoric acid; these reactions are not acid catalyzed, and reaction rates increase with a rise in pH. (30) By contrast, rate-determining migration step 2 (Eq. 1) is suggested by $\rho = -2.55$ (σ) for the peroxomonophosphoric acid oxidation of substituted acetophenones in acetonitrile. (28) Also, similar activation energy data for peroxomonosulfate oxidation of dialkyl ketones in aqueous acetic acid have been used to support rate-determining rearrangement step 2. (24)

Oxidation of the 1,2-diketone *o*-quinone with isotopically labeled hydrogen peroxide under basic conditions indicates that the normal two-step Baeyer–Villiger mechanism is followed for C - C bond cleavage. (31) It is notable that Hammett correlations of the reactions of substituted benzils indicate the limitations inherent in the use of the sign of ρ values for the assignment of mechanism. For a reaction with a rapid preequilibrium step followed by a slower migration, the observed rate depends on both the equilibrium constant for formation of the Criegee intermediate and the rate of the migration step (Eq. 2). (32) The noncatalyzed rearrangement of substituted benzils with peracetic acid in acetic acid has a $\rho = +1.51$ (σ), while the sulfuric acid catalyzed rearrangement has a $\rho = -0.67$ (σ). The change in sign may be consistent with rate-determining addition in both cases. The positive ρ in the absence of catalysts reflects the ability of electron-withdrawing groups to facilitate attack by nucleophilic peroxide oxygen on the carbonyl group. The negative ρ with acid catalysis is postulated to reflect an increase in the value of the equilibrium constant *K* as electron donation facilitates protonation of the benzil (Bz_2) carbonyl group. (33) Similar arguments might be made to support migration in the adduct as rate-determining.

$$
\begin{aligned}
&Bz_2 + H^+ \overset{K}{\rightleftharpoons} Bz_2H^+ \\
&Bz_2H^+ + AcO_2H \xrightarrow{k} \text{Adduct} \\
&[Bz_2H^+] = K[H^+][Bz_2] \\
&\text{rate} = k[Bz_2H^+][AcO_2H] = kK[H^+][Bz_2][AcO_2H]
\end{aligned}
\tag{2}
$$

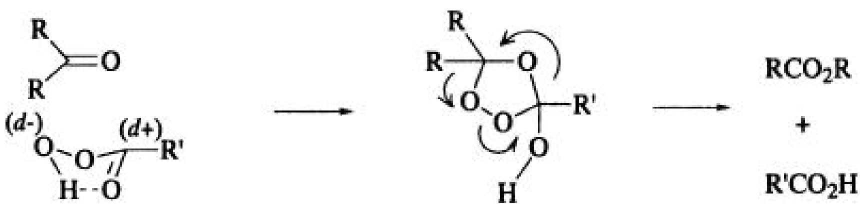
2.5. Alternative Mechanisms

Exceptions to the above generalizations of a two-step ionic mechanism with step 2 migration as rate determining have been suggested. Although a plot of the trifluoroacetic anhydride catalyzed oxidation of *p*,*p′*-substituted benzophenones in refluxing methylene chloride versus σ^+ is linear with a $\rho = -0.77$, supporting the ionic mechanism, when peracetic acid is the oxidant there is not a Hammett plot correlation. The relative rate results in Table 1 for these oxidations fit the rate at which aryl radicals attack aromatic rings. Although a mechanism involving a carboxylate radical is implicated under this set of conditions, no carbon dioxide evolution is observed. (34)

Table 1. Relative Rate Data for Oxidation of *p*,*p′*-Unsymmetrically Substituted Benzophenones

	Peracid	
Substituent	**TFPAA**	**PAA**
OCH_3	211	152
CH_3	26	9
NO_2	1	3.2
Br	14	2
Cl	12	1.2

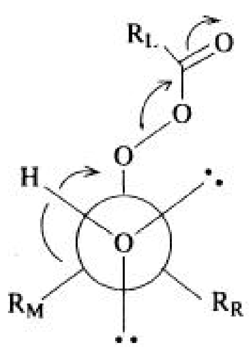
A concerted 1,3-dipolar mechanism has been suggested (Eq. 3). (35) It has been used to rationalize rate law data for the peroxymonophosphoric acid (PMPA) oxidation of cycloalkanones. (25) The results of ^{18}O-tracer experiments implicate dioxiranes as intermediates in the oxidation of cyclohexanone and acetophenone with bis(trimethylsilyl)peroxomonosulfate. (36)



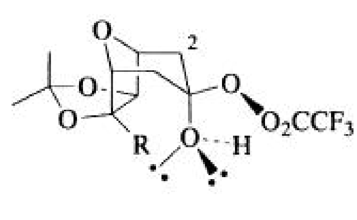
(3)

2.6. Stereoelectronic Effects

Stereoelectronic requirements proposed for the migration step are antiperiplanar arrangements between both a nonbonding electron pair on oxygen and the O - O bond with the bond of the migrating carbon atom as in **6**. (9, 37-40) These prerequisites and considerations of nonbonded steric interactions between R and hydroxy hydrogen have accounted for the observed preference of C-2–methylene migration from conformer **7**. (38, 40)

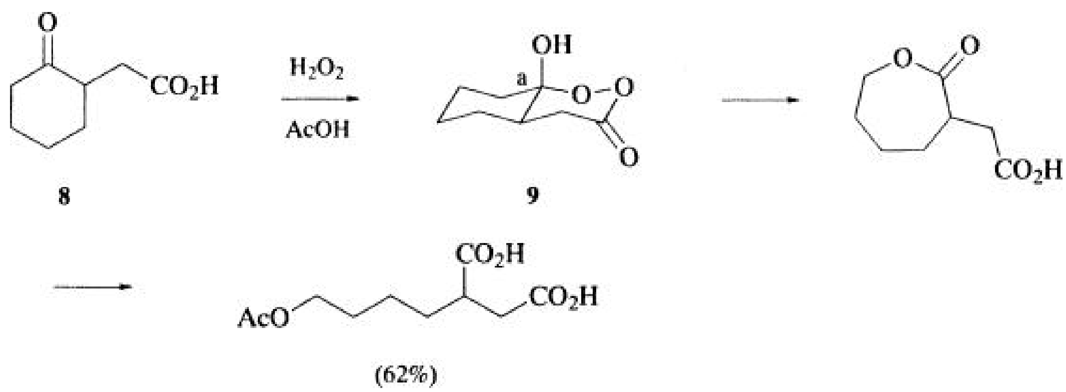


6



7

Evidence for a stereoelectronic effect in an intramolecular Baeyer–Villiger reaction was found in the preferential migration of the methylene carbon during oxidation of cyclohexanone **8**. Assuming rearrangement occurs from the rigid *trans*-fused intermediate **9**, only bond **a** can assume the proper antiperiplanar orientation for migration. (37)



3. Scope and Limitations

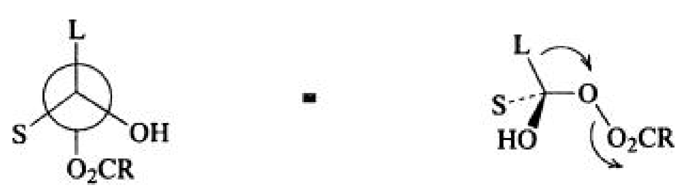
3.1. Reactions of Straight-Chain Ketones

3.1.1.1. Oxidation of Dialkyl Ketones

Migratory ability of alkyl groups in acid catalyzed Baeyer–Villiger reactions decreases in the orders tertiary > secondary > primary > methyl, (15, 41-44) and benzyl > primary > methyl. (16, 21) Migratory aptitudes of cyclopropyl ketones with MCPBA or TFPAA are phenyl = secondary > primary > cyclopropyl > methyl. (42, 45) Ketones of the type RCH_2COCH_2R, which have only primary alkyl groups attached to carbonyl, are unreactive with perbenzoic acid and peracetic acid, (46) but they do undergo oxidation with the reactive trifluoroperacetic acid, (42) bis(trimethylsilyl)monoperoxysulfate, (47) potassium persulfate in sulfuric acid, (41) and with 90% hydrogen peroxide/boron trifluoride etherate. (46) A method for preparation of α -deuterated acids and alcohols which avoids the use of deuteride reducing agents involves catalyzed deuterium exchange alpha to carbonyl and then cleavage with TFPAA (Eq. 4). (48, 49)

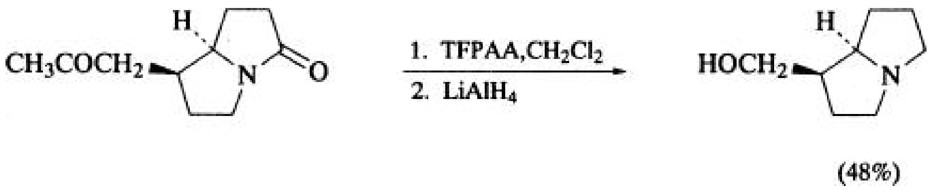
$$CH_3CD_2COCD_2CH_3 \xrightarrow{\text{TFPAA}} \underset{(64\%)}{CH_3CD_2CO_2H} + CH_3CD_2OH \qquad (4)$$

The migratory trend in Baeyer–Villiger oxidations has been attributed to electronic and conformational factors. Groups which can best support a positive charge by induction or hyperconjugation are more likely to migrate. It has also been suggested that migration occurs from a favored rotamer **10**, which has the bulkier group antiperiplanar to the leaving group. (15)



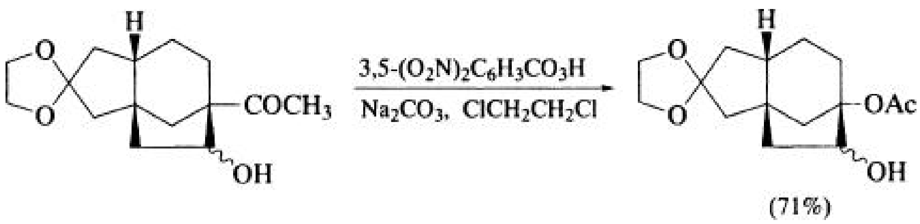
10

Since methyl is a poor migrator, the Baeyer–Villiger reaction has been used extensively to convert methyl ketones to acetate esters while shortening a carbon chain by two units. (50-54) The method is of broad utility, since methyl ketones can be derived from carboxylic acids (55-60) and methyl-substituted olefins. (50, 61-64) The Baeyer–Villiger oxidation was utilized to shorten the carbon chain in a synthesis of the alkaloid isoretronecanol (Eq. 5). (65)



(5)

Baeyer–Villiger oxidation of methyl ketones has played a major role in a number of novel synthetic transformations. Examples include the introduction of a bridgehead hydroxy group following use of an acetyl functionality in an aldol condensation in the synthesis of gibberellic acid (Eq. 6). (66) The Woodward reserpine precursor



(6)

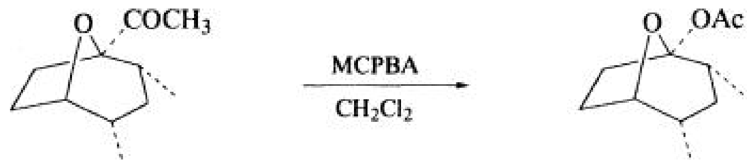
12, the acetate of a β -hydroxyester required for a ring-cleavage reaction, was prepared from the β -acetyl compound **11**. (67)

11

12 (59%)

Ether or alcohol oxygen, (61, 68-72) and amine (73) or, less effectively, acylated nitrogen (74) atoms alpha to the carbonyl aid migration and accompanying chain cleavage during peracid reactions. MCPBA oxidation of the acetylfuran derived cycloadduct **13** provided the acetate of a 4-hydroxycycloheptanone hemiketal **14** needed in a stereocontrolled strategy for synthesis of the Prelog–Djerassi lactone and similar macrolide antibiotics.

([75]) Oxidation of the acyl β -lactam **15** was part of a synthesis of the penam and carbapenem intermediate **16** from D-allothreonine and *trans*-crotonic acid. ([55])

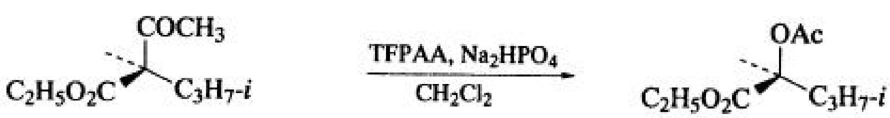


13 **14** (60%)

15 **16** (90%)

Peracid treatment of acyclic 1,3 diketones can give complex reaction mixtures from α -hydroxylation, ([76]) cleavage of both acyl groups, ([76], [77]) and molecular rearrangements. [78,78a]

However, the α -acyl ester **17**, which lacks an acidic methylene hydrogen, can be converted to an α -acetyl ester with TFPAA. ([79]) Reaction of peracid with the enol form of a 1,3-dicarbonyl compound is suppressed by the α -directing ether substituent in ethyl 4-ethoxy-3-ketobutyrate, and diester **18** is obtained with MCPBA. ([79a])

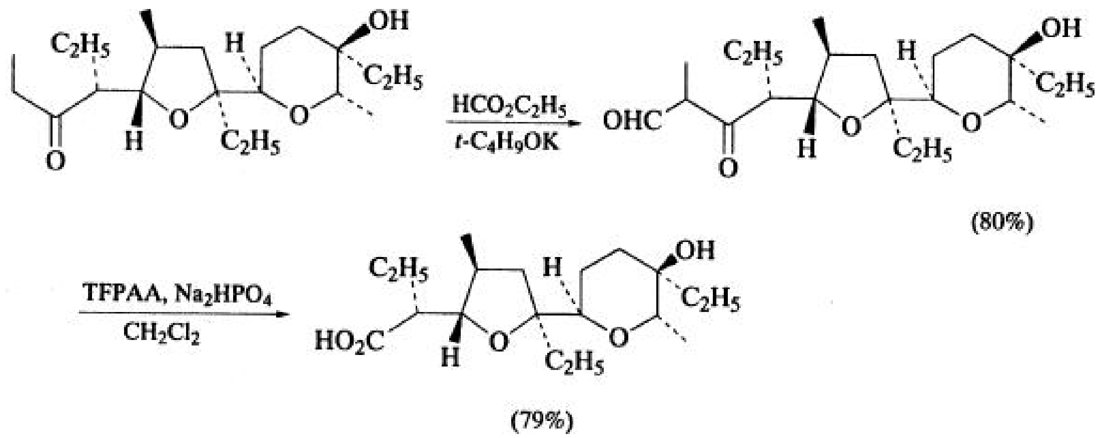


17 (89%)

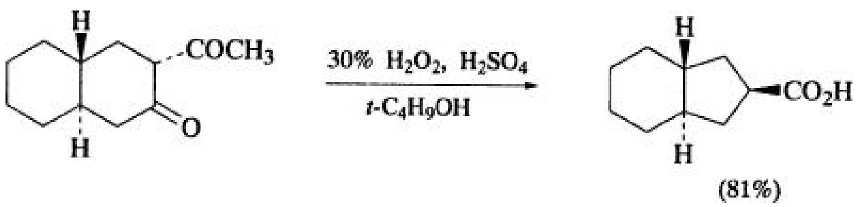
$$C_2H_5OCH_2COCH_2CO_2C_2H_5 \xrightarrow[CHCl_3]{MCPBA} C_2H_5OCH_2O_2CCH_2CO_2C_2H_5$$

18 (70-80%)

A novel method of directed chain shortening by an α substituent involves initial introduction of a formyl group alpha to a ketone and subsequent oxidation with TFPAA (Eq. 7). ([80]) Acidic 30% hydrogen peroxide treatment of an α -acetyl cyclic ketone results in a ring-contracted carboxylic acid (Eq. 8). ([81], [82])

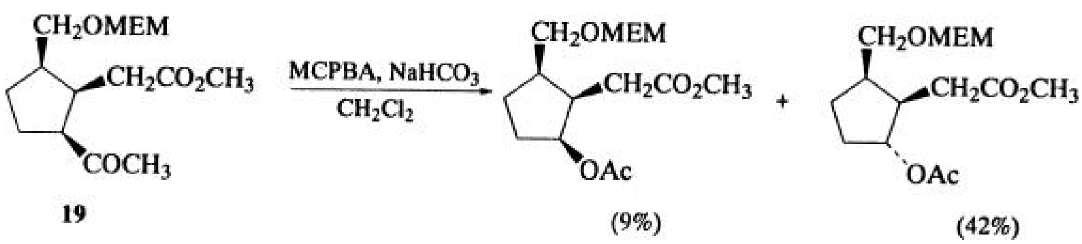


(7)

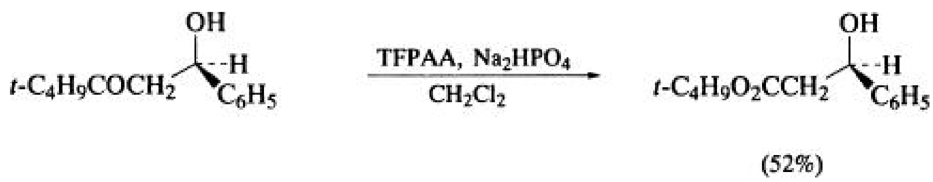


(8)

A rare example of partial epimerization of acetyl prior to oxidation has been observed for the sodium bicarbonate catalyzed MCPBA reaction with the hindered cyclopentyl substrate **19**. A mixture of *cis* and *trans* acetates was isolated. The *trans*-acetyl isomer of **19** reacts normally. (83)

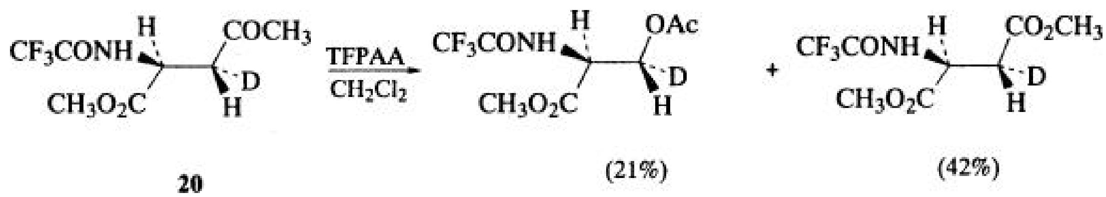


Complementary to the use of methyl as a nonmigrating group is the use of *tert*-butyl as a preferentially migrating ligand. (84) Normally, oxidation of β -hydroxy methyl ketones gives preferential migration toward the hydroxy group to form 1,2-diol monoesters. (85) However, β -hydroxy *tert*-butyl ketones oxidize to *tert*-butyl esters of β -hydroxycarboxylic acids (Eq. 9). (86)

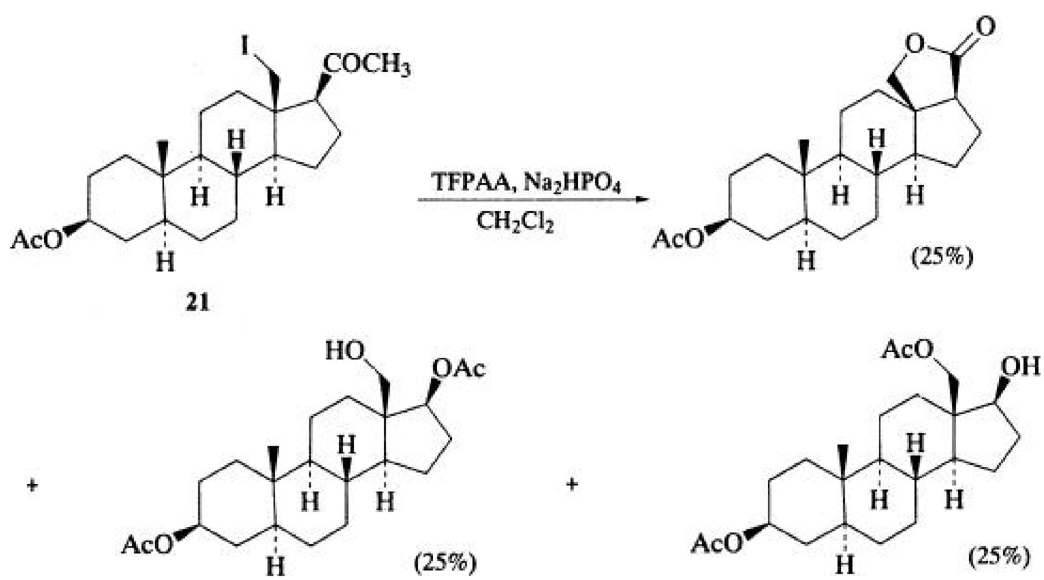


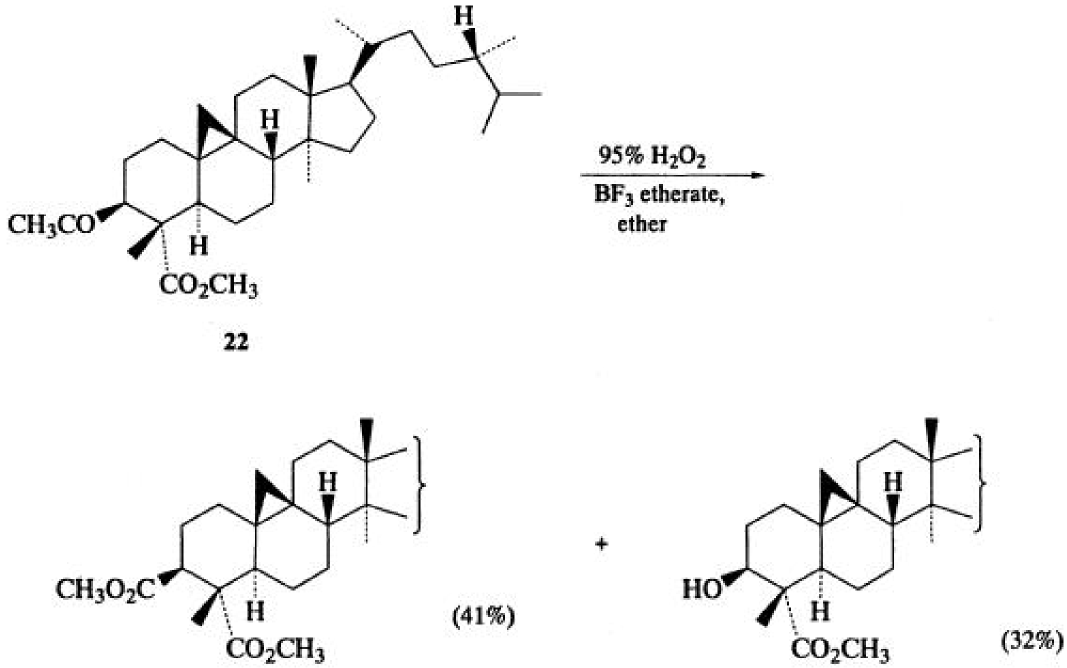
(9)

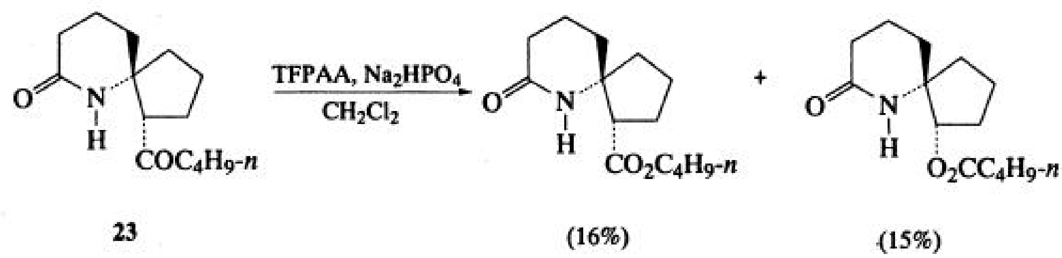
The bias against methyl migration has been overcome when migration of one group is retarded. In the oxidation of aminoester **20** the strongly electron-withdrawing ester and *N*-acyl groups decrease the migratory ability of the proximate methylene (67:33 bias for methyl migration). (87-90)



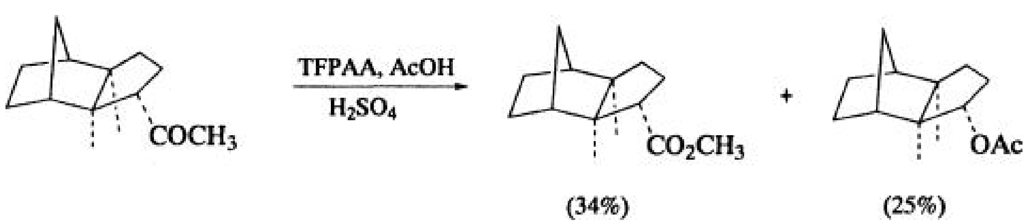
Significant amounts of methyl migration have been observed even when the competition is with a secondary alkyl group. Examples include the oxidations of 18-iodo-20-ketosteroid **21** (1:2 methyl:secondary carbon migration) (91) and 3-acetyl-4-methoxycarbonyl steroid **22** (41:32 methyl:secondary carbon migration. (51) Primary alkyl migrates in preference to secondary alkyl in the spiro-amide **23**. (92)







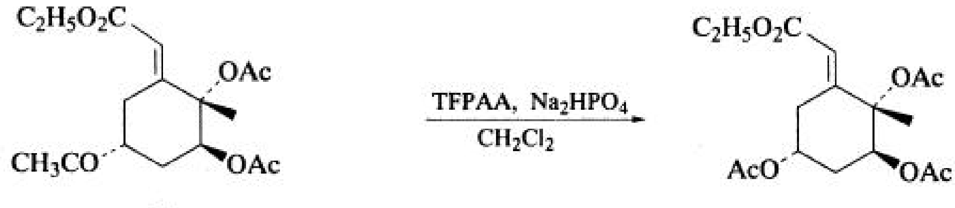
Migration of the smaller group is a likely consequence of substituent electron-withdrawing effects, since conformational considerations should have resulted in migration of the bulkier group in these highly crowded substrates. (15) Nevertheless, there is one example in which crowding favors methyl migration (Eq. 10). (93)

 (10)

Migration can be enhanced by a β -silicon substituent, and the proximal primary alkyl group of **24** migrates in preference to the distal secondary one. The migratory aptitude of β -trimethylsilylethyl is intermediate between that of secondary and tertiary alkyl groups. (94)

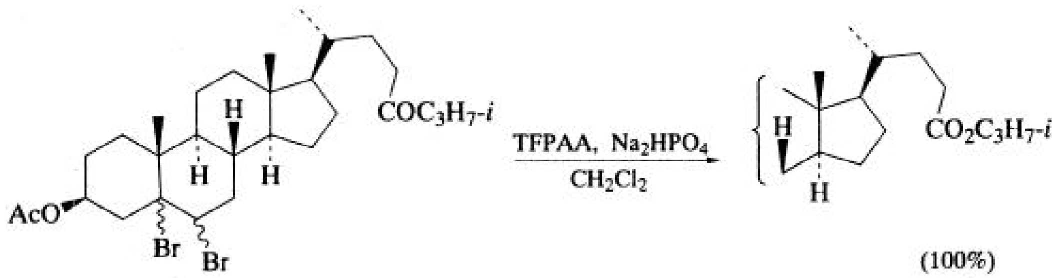
$$\underset{\mathbf{24}}{(CH_3)_3Si(CH_2)_2COC_3H_7\text{-}i} \xrightarrow[CH_2Cl_2]{MCPBA,\ Na_2HPO_4} (CH_3)_3Si(CH_2)_2O_2CC_3H_7\text{-}i\ (53\%) + (CH_3)_3Si(CH_2)_2CO_2C_3H_7\text{-}i\,(27\%)$$

Chemoselective Baeyer–Villiger oxidations can occur in the presence of amino acids, (95, 96) amines, (97) pyridines, (98, 99) or anilines. (97) However, 3-acetylpyridine forms only the *N*-oxide with MCPBA. (100) Chemoselectivity in the presence of olefins depends upon structure and oxidizing agent. Chemoselective olefin oxidation of non-conjugated acyclic enones with organic peracids is generally faster than the Baeyer–Villiger reaction. (101-104) Electron-poor olefin **25** undergoes a Baeyer–Villiger reaction with TFPAA. (105) A reactive double bond can be protected as its dibromide, as in the oxidation of the steroid **26**. (104) Basic hydrogen peroxide, which doesn't attack isolated olefins, cleaves the isopropyl group of **27** in preference to the tertiary substituent bearing a carboxylate anion. (106)

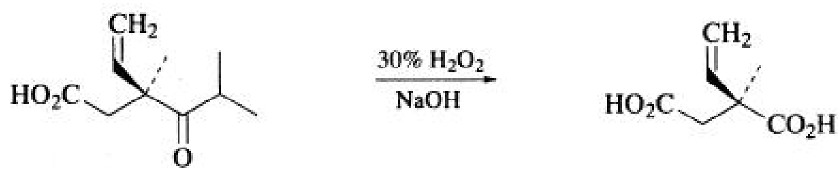


25

(>75%)



26



27

(100%)

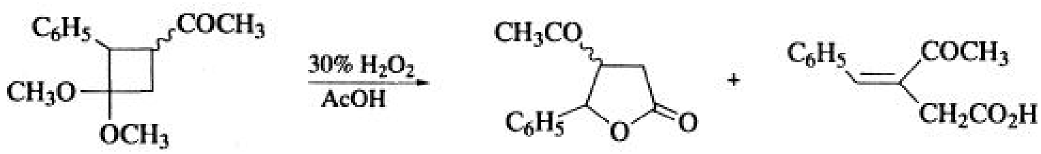
Carbonyl group selectivity is observed for MCPBA oxidation of a side chain acetyl in preference to a hindered ring carbonyl in cyclic ketone **28** (107) and hindered 11-ketosteroids. (108, 109) However, the ring carbonyl of **29** reacts. (110) Deketalization of **30** and peracetic acid oxidation of the derived cyclobutanone occurs in preference to oxidation of the side-chain acetyl. (111)

28

(77%)

29

(79%)



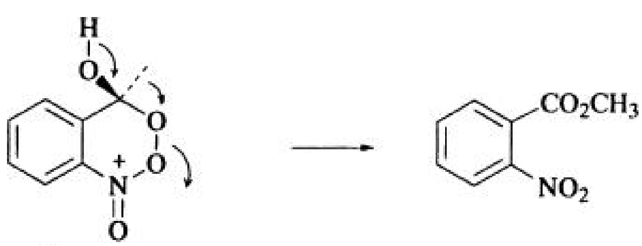
30

(95%)

3.1.1.2. Oxidation of Aryl Alkyl Ketones

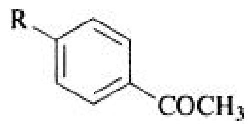
Aryl alkyl ketones can undergo Baeyer–Villiger oxidation with migration of either substituent depending upon the functional groups on the aryl ring, structure of the alkyl group, and choice of oxidizing reagent and conditions. (2) Relative migratory aptitudes for phenyl alkyl ketones using buffered TFPAA are tertiary > secondary = benzyl > phenyl > primary > methyl. (15, 112)

Substituents on an aryl group slightly decrease the amount of aryl migration as shown in Table 2. (15, 28, 29, 113) The large preference for methyl migration over an *o*-nitrophenyl group could be related to partial participation by nitro group oxygen in cleavage of the O - O bond to form an intermediate peroxide **31**. The methyl group, but not the aryl ring, can achieve the proper *anti* alignment required for the migration step. (113)



31

Table 2. TFPAA Oxidation of Substituted Acetophenones

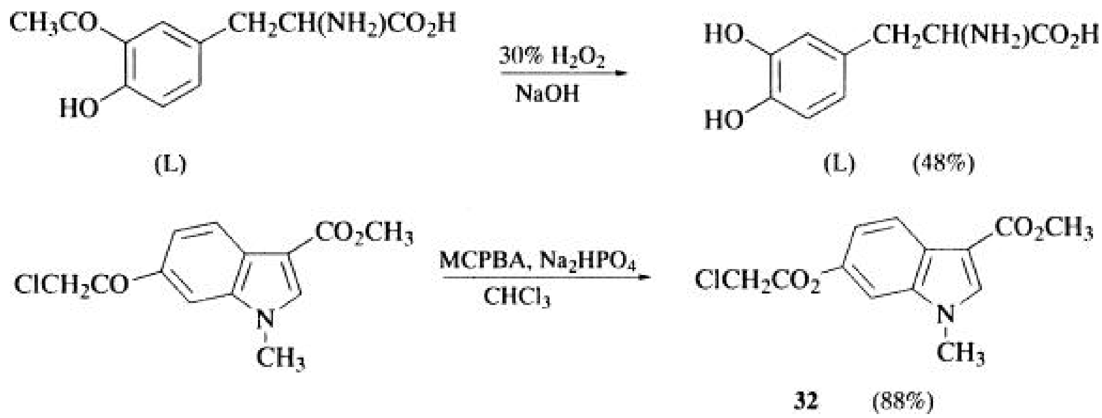


Substituent R	Aryl Migration (%)	Yields (%)	Ref.
p-NO_2	87	67	15, 113
m-NO_2	63	100[a]	113
o-NO_2	6	38	113
H	100	100	113
Cl	97	36	15
CF_3	82	73	113
CO_2H	97	86	113
CO_2CH_3	97	77	113
OCH_3	88	75[a]	113

[a]The yield was determined by titration.

Weaker peracids afford greater reaction regioselectivity. For phenyl cyclohexyl ketone the weaker peracid peracetic acid (10% phenyl migration) is more selective for aryl migration than is TFPAA (20% phenyl migration). (15) Sodium perborate is selective solely for aryl migration with *p*-methoxy-, *p*-bromo-, *p*-phenyl-, or *p*-methylacetophenone. (114) Steric effects have been studied for the Dakin oxidation of *o*- and *p*-acylphenols with hydrogen peroxide/sodium hydroxide. Larger alkyl groups on the carbonyl slow the reaction. (115)

The preference for aryl over primary alkyl migration allows acylated aromatic rings to be converted to phenols. (116, 117) The oxidation of a C-2 acyl group on an aromatic A-ring is chemoselective in the presence of a steroidal 17-ketone. (118, 119) A two-step procedure of acylation followed by Baeyer–Villiger oxidation has been used to convert L-tyrosine to L-dopa (Eq. 11). (95) It was necessary to use the chloroacetyl group in order for the Baeyer–Villiger reaction to proceed as desired to prepare the oxygenated indole ring **32**. (120, 121)



(11)

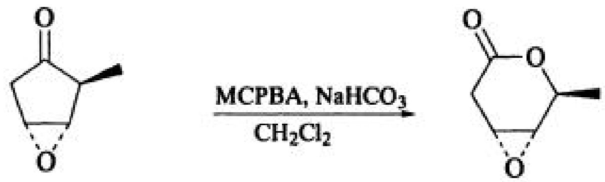
When oxidations of acetophenones are carried out using *tert*-butylhydroperoxide/potassium hydroxide in chlorobenzene, benzoic acids derived from preferential primary, secondary, or tertiary alkyl migration are obtained rather than phenols. Unlike the peracid mediated Baeyer–Villiger oxidation, electron-withdrawing substituents on the aryl ring increase the reaction rate. Diaryl ketones do not undergo the oxidation. The reaction does not involve radicals since there is no induction period and no inhibition by the radical scavenger arsenious acid. (122-124)

3.1.1.3. Oxidation of Diaryl Ketones

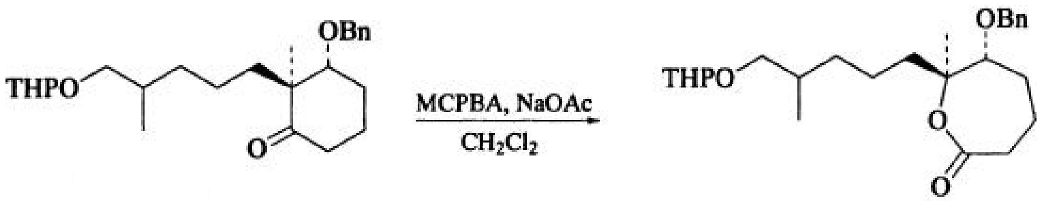
In the cleavage of unsymmetrical diaryl ketones the more electron-releasing group normally migrates. (2) With mono-*p*-substituted benzophenones the migratory order is H > Br > Cl > NO_2. (20) An *ortho* effect has been noted; *p*-chlorophenyl migrates in preference to an *o*-chlorophenyl, and an *o*-methylphenyl hinders migration relative to phenyl. An *o*-methoxyphenyl group still migrates preferentially. (125) A dibenzocyclobutane migrates in preference to phenyl. (126, 127)

3.2. Reactions of Monocyclic and Spirocyclic Ketones

Oxidation of cyclic ketones to lactones is useful in the synthesis of heterocycles as shown by the formation of **33**, a precursor of the carbohydrate daunosamine, (128) and **34**, a precursor of the cyclic ether ring of zoapatanol. (129)

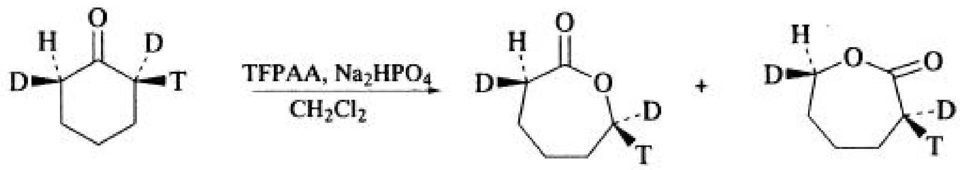


33 (98%)

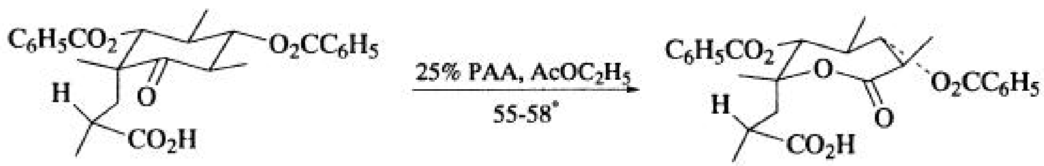


34 (70%)

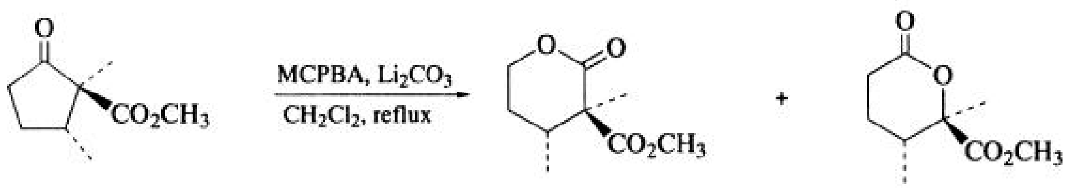
An extensive use of the Baeyer–Villiger reaction is in the stereocontrolled synthesis of carbon chains by ring opening of the lactones derived from stereoselectively functionalized cyclic ketones. (130-142) By this method chiral 2-deuterio-2-tritioacetic acid was synthesized from the chiral ketone **35**. (143) In the total synthesis of erythronolide **B** regioselective ring opening of a substituted cyclohexanone **36** provided the hydroxyacid precursor **37**, (144) and a stereocontrolled synthesis of the diester side chain of integerrinecic acid used the major isomer **39** formed upon oxidation of the cyclopentanone **38**. (145)



35 (>85% of the mixture)



36 37 (70%)



38 (13%) (77%) 39

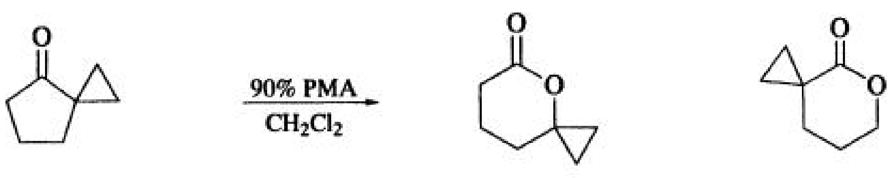
Cyclobutanones are especially reactive and can be ring expanded not only with customary organic peracids, (146) but also with hypochlorous acid (147) or alkaline hydrogen peroxide at room temperature. (148) Rates of oxidation of some cyclic ketones with perbenzoic acid are shown in Table 3. (149) The effect of bulky substituents near the carbonyl is to lower the rate by decreasing the equilibrium constant for formation of the Criegee intermediate (Eq. 1). Steric effects account for the selective oxidation of the side-chain carbonyl in ketone **28**, (110) but the ring ketone in the *trans*-monomethyl ketone **29**. (107) The oxidation rate for the medium ring cyclodecanone is retarded relative to the rates for cyclohexanone or cyclopentanone.

Table 3. Oxidation of Selected Ketones with Perbenzoic Acid (25°, Chloroform)

Ketone	Rate ($k \times 10^{-4}$ L mole^{-1} s^{-1})

Cyclopentanone	2.2
3-Methylcyclopentanone	1.4
Cyclohexanone	15.8
2-Methylcyclohexanone	7.5
2,2-Dimethylcyclohexanone	5.0
3-Methylcyclohexanone	12.2
4-Methylcyclohexanone	19.2
4-*tert*-Butylcyclohexanone	27.7
2-Chlorocyclohexanone	0.4
Cyclodecanone	0.1

The regiochemistry of oxygen insertion follows the principles set out for oxidation of open-chain ketones. There is a customary preference for migration of the α substituent which has the most alkyl substituents. This is true for ring sizes of four, (146, 150-153) five, (128, 133, 134, 154-166) six, (110, 129, 135, 137, 138, 140, 167-173) seven, (174) nine, (131) and twelve carbons. (175-178) An α -phenyl group facilitates migration, (179-182) as do α-benzyl (183) and α-allyl groups. (102, 120, 130, 184) In contrast to the preference in openchain ketones, the major product **41** isolated in the permaleic acid (PMA) oxidation of **40** is formed by migration of the spirocyclopropyl carbon. (185) The spiro carbon also migrates in α -spirocyclobutanones, (148, 186-193) even if electron-withdrawing β -bromo, (194) β -hydroxy, (194, 195) or β -*tert*-butyldimethylsilyloxy (194, 195) groups are present on the adjacent ring.

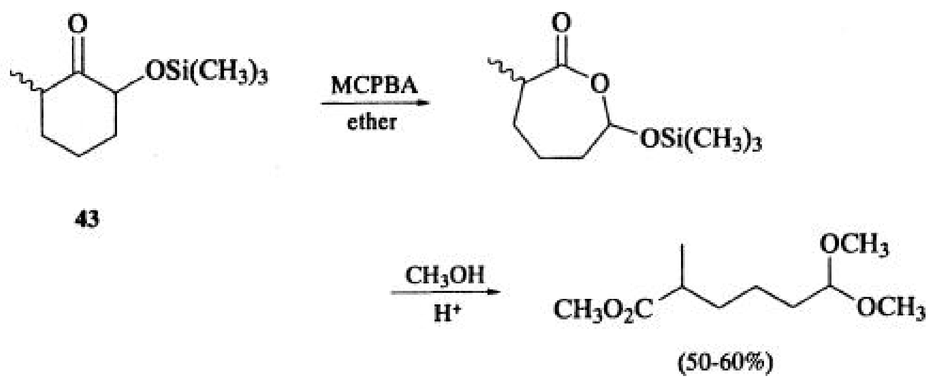


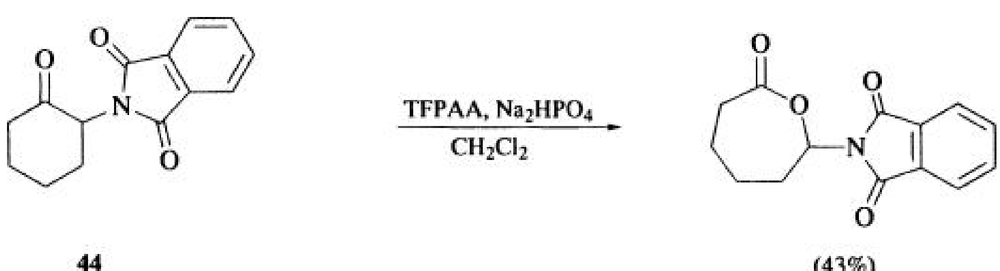
40 **41** **42**

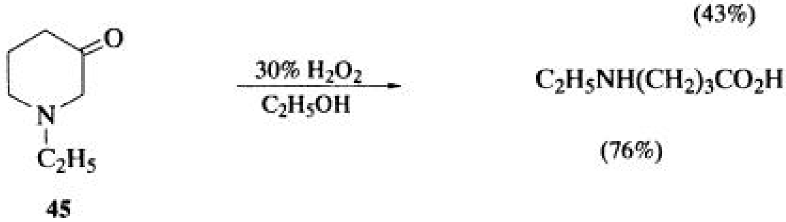
41:**42** = 89:11

Steric hindrance toward attack by peracid on the carbonyl group can stop oxidation. Although 2-chloro-2,4,4-trimethylcyclobutane-1,3-dione reacts with peracetic acid, no reaction occurs if the 2 methyl is replaced by isopropyl. (153) The medium ring compound cyclodeca-1,6-dione is unreactive with MCPBA after 31 days at 25° or 45 hours at 45°. (196)

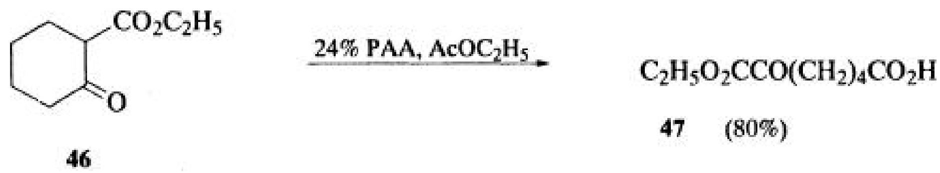
Migration is favored by α -ether (197, 198) and α -acetate (199, 200) groups, and an α -trimethylsilyloxy group directs migration in preference to a methyl group in **43**. (197) An α -*N*-methyl-*N*-tosyl group (198a) is directing in the same manner as the imide group is directing in the oxidation of **44**, (201) while the α -amino group of **45** facilitates cleavage of the ring. (73) An α -chloro group normally retards migration. (153) If TFPAA is the oxidant, 2-chlorocyclohexanone gives an α -chlorolactone, (201) but adipic acid, which arises by cleavage at the chlorine bearing carbon, is formed using perarsenious acid on polystyrene. (182)



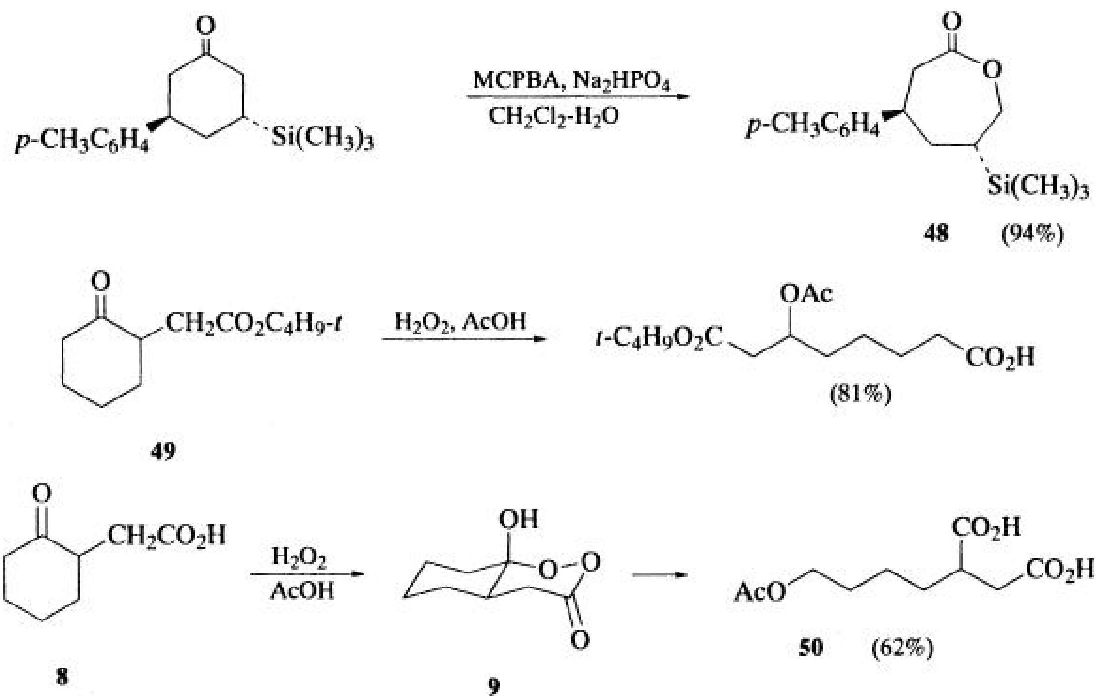




Cyclic α -acyl ketones undergo ring contraction and ring cleavage reactions with neutral or basic hydrogen peroxide; (78, 202-204) Peracetic acid converts **46** to **47**. (205) The electron-withdrawing α-ester substituent in **38** does not block regioselective Baeyer–Villiger oxidation toward the alkyl group to give **39**. (145, 206)

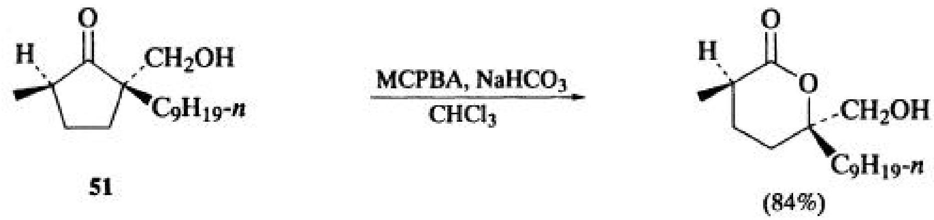


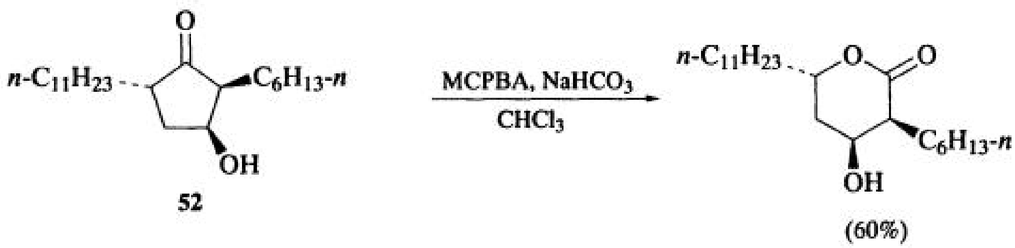
The directing effect of a β -trimethylsilyl group (139, 207) is impressive as shown by the totally regioselective formation of lactone **48**. (208, 209) Silyl lactones are useful in the synthesis of olefinic esters and acids. (94) A β -alkoxycarbonyl substituent does not retard migration of the proximal alpha carbon in the peracetic acid oxidation of ketone **49**. (37) The β -carboxylic acid in ketone **8** effects an intramolecular Baeyer–Villiger

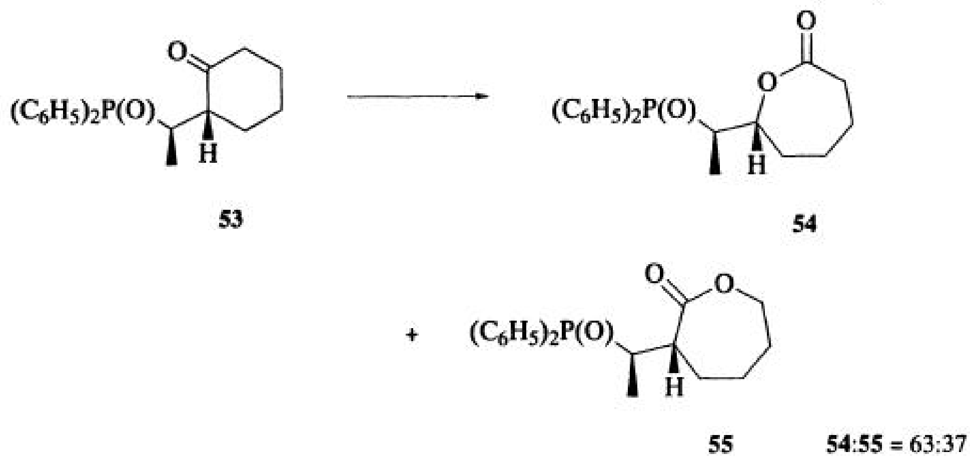


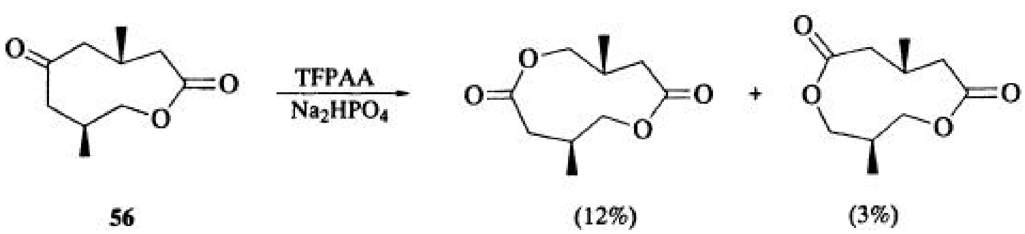
reaction via **9** to give **50**; only the distal methylene in **9** can assume the proper orientation for migration. (37) Oxidation of the *tert*-butyldiphenylsilyl ether of α -hydroxymethylcyclopentanone (209a) and ketone **51** with MCPBA both occur with migration toward the β -hydroxy group, (166) while β -hydroxyketone **52** gives solely lactone derived by migration of the methine away from the β -hydroxy group. (209b) Hydrogen peroxide results in β -elimination and cleavage of 2-aminomethylene ketones at the 2 position, (158) but oxidation can proceed further as in the conversion of 2-isopropoxymethylcyclohexanone to adipic acid. (204) The directing effect of a β -phosphine oxide group on a

C-2 alkyl side chain of **53**, although oxidation results in major C-1 migration to give **54**, is affected by the stereochemistry of a methyl group at C-1. (210) The methyl epimer of **53** gives 96% insertion adjacent to the side chain. The combined influence of α -carbonyl and oxygen substituents in ketolactone **56** results in preferential migration of the carbon away from oxygen. (211)

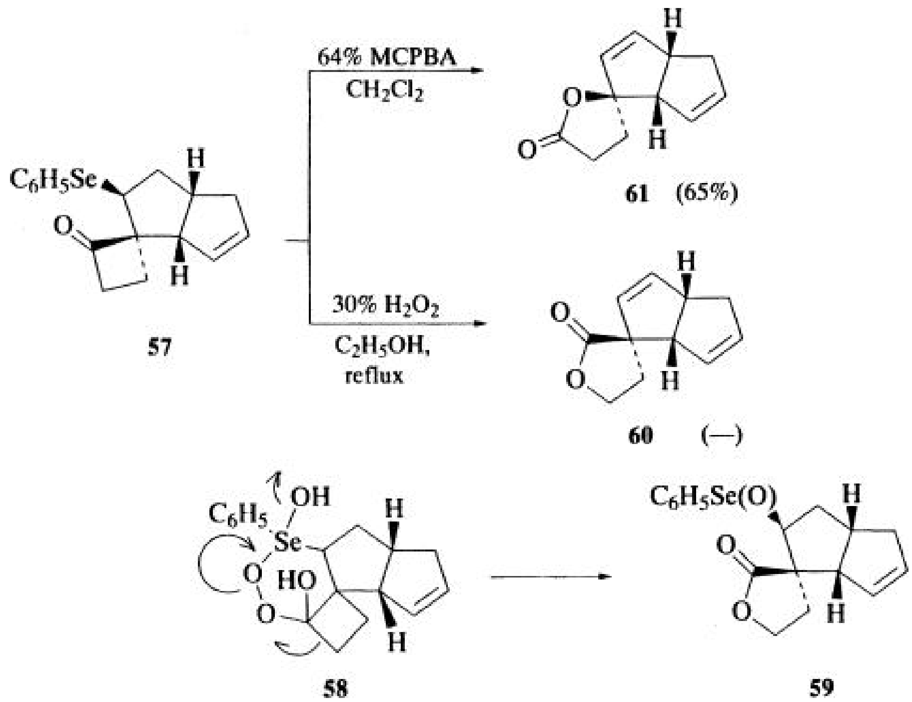






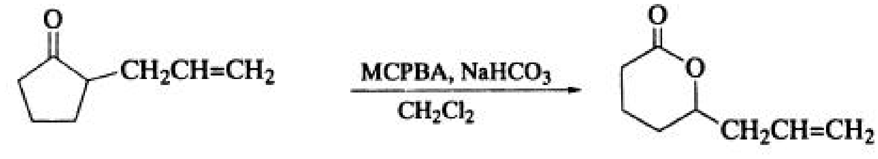


A neighboring β -selenium substituent influences the regiochemistry of oxidation of the spirocyclobutanone **57**. With hydrogen peroxide in ethanol initial oxidation to selenoxide enables formation of a cyclic peroxide **58**. Geometric constraints force migration of the methylene group to give **59** and then lactone **60**. When hydrogen peroxide/potassium carbonate, (212) for which Baeyer–Villiger oxidation is faster than selenium oxidation, or MCPBA, which cannot form a cyclic peroxide, are used as oxidants, the usual bridgehead migrated lactone **61** is obtained. (195, 213)

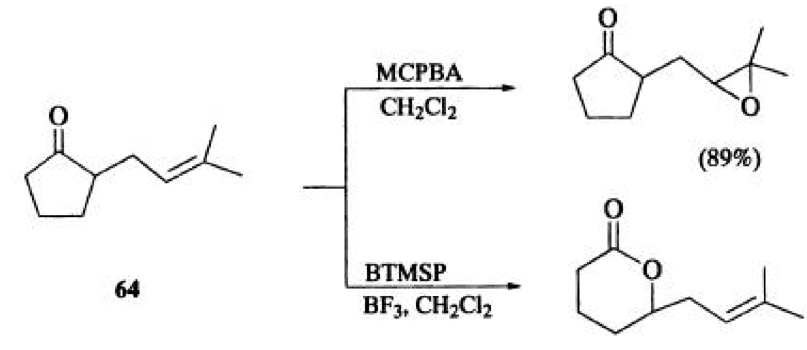


Chemoselective oxidations of α -thioether (214, 215) and α -phenylselenenide (216) ketones occur on the heteroatoms. Vinylsilanes form epoxysilanes (217) and α -diazoketones form 1,2-diketones with MCPBA. (218) Chemoselectivity favoring Baeyer–Villiger reaction for nonconjugated enones depends upon the relative reactivities of the carbonyl and olefin and the choice of oxidant. (184) Reactive four-membered rings undergo only ring expansion with 30% hydrogen peroxide/sodium hydroxide. (148, 187, 195, 212, 213) Ring expansion is also generally found with cyclobutanones and organic peroxides; (151, 187, 195, 213) however, oxidation of spirocyclobutanone **62** is an exception. (219)

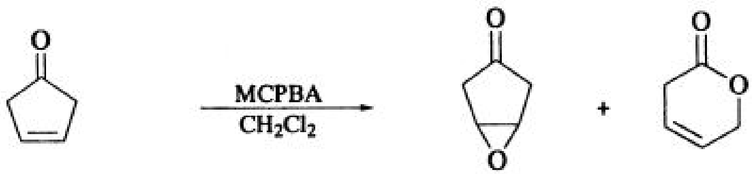
Allylcyclopentanone **63** undergoes Baeyer–Villiger oxidation with MCPBA. (130) Although the dimethylallylcyclopentanone **64** reacts preferentially on the double bond with MCPBA, bistrimethylsilyl peroxide (BTMSP) with boron trifluoride



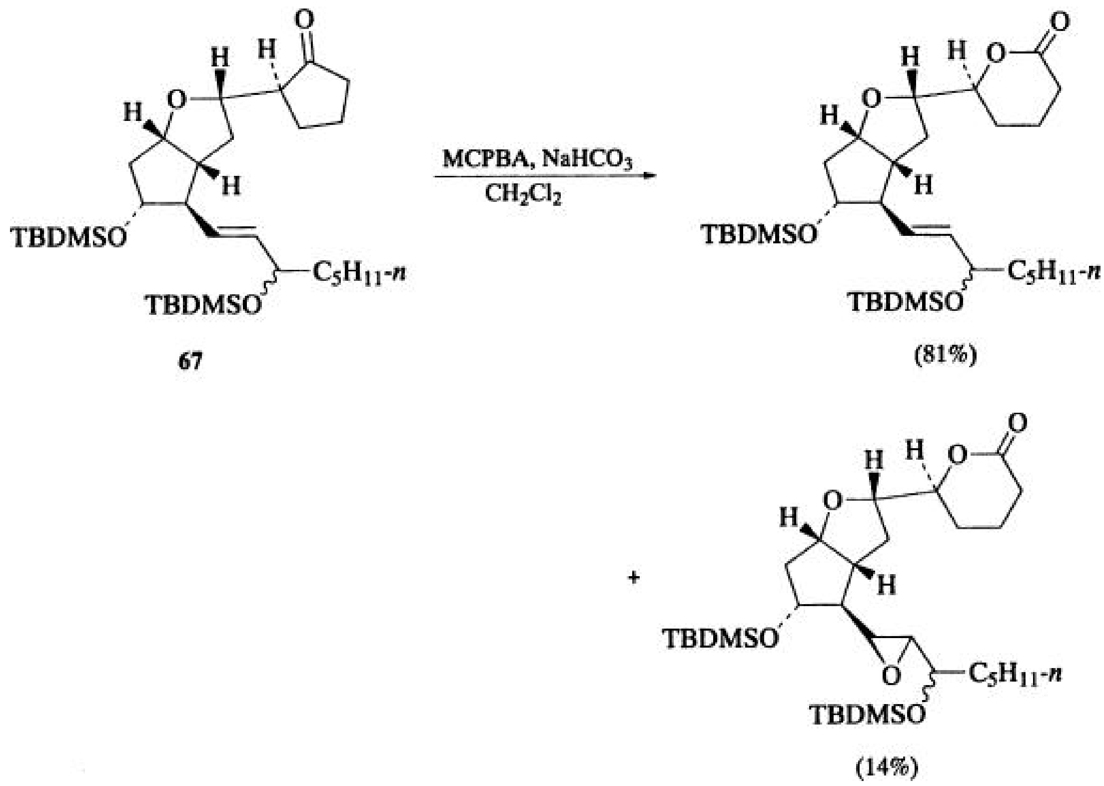
63 (55%)



64 **65** (44%)

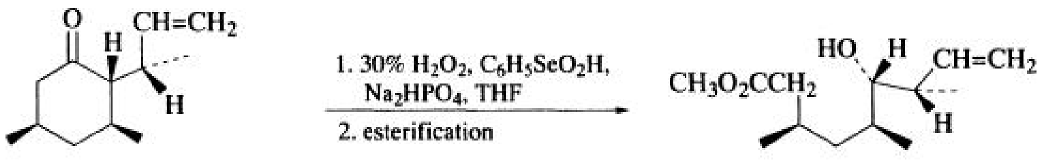


66 (63%) (6%)



67 (81%) (14%)

catalyst affords the lactone **65**. (220) Cyclopentenone **66** also affords mainly epoxide with MCPBA. (221) It has been postulated that steric hindrance provided by an allylic *tert*-butyldimethylsilyloxy group hinders epoxidation and favors Baeyer–Villiger oxidation of ketone **67**. (161) Although 2-allylcyclohexanone undergoes Baeyer–Villiger reaction with peracetic acid, (184) it is necessary to use perseleninic acid to carry out the ring cleavage of ketone **68**. (222)



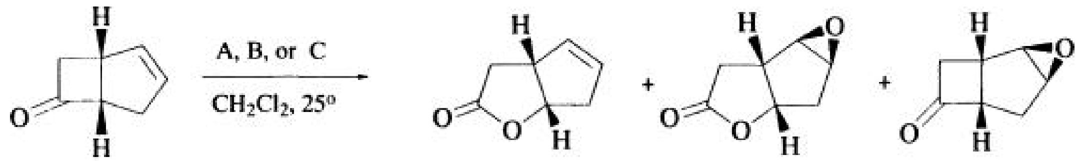
68

(63%)

3.3. Reactions of Fused-Ring Ketones

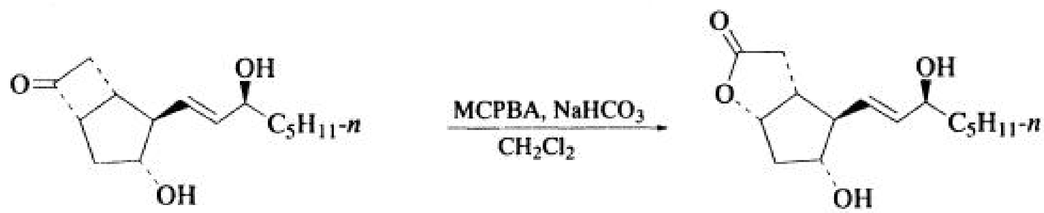
3.3.1.1. Oxidation of Alicyclic Ketones

Cyclobutanones are reactive under a variety of Baeyer–Villiger conditions, and chemoselective oxidations in the presence of cyclohexanones can be affected with peracetic acid (111) or basic *tert*-butyl hydroperoxide. (223) Lactone formation in the presence of olefins often can be carried out with hydrogen peroxide/acetic acid (224, 225) or limited amounts of organic peracids. (226-229) Reaction of MCPBA, which gives high Baeyer–Villiger selectivity with ketone **69**, (230) provides the prostaglandin precursor **70**. (231) Although not always effective in carrying out the Baeyer–Villiger oxidation, (232) a better method to avoid olefin epoxidation is to use basic hydrogen peroxide (233) or alkyl peroxide solutions, (234) as in formation of the lactone **71**, an eriolanin and eriolangin precursor. (235) Basic hydrogen peroxide is effective for oxidation of a cyclobutanone even in the presence of a conjugated ketone. (187, 236)

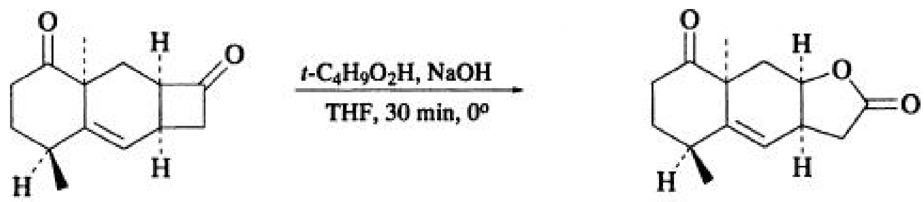


69

	I	II	III
A = MCPBA	(95.3%)	(2.8%)	(1.4%)
B = $Cl_3CCH_2CO_3H$	(28%)	(41%)	(31.3%)
C = $C_2H_5OCO_3H$	(69%)	(21%)	(9.4%)



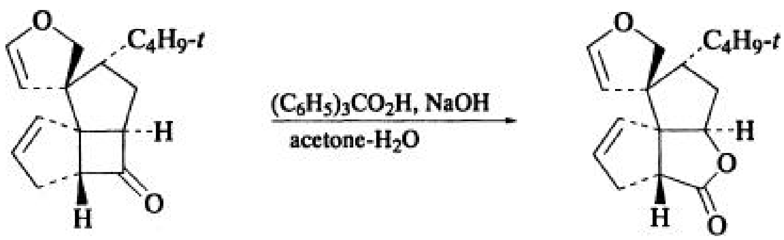
70 (86%)



71 (83%)

The regiochemistry of oxidations of fused-ring cyclobutanones is usually toward the bridgehead. (237) However, nonbridgehead substitution in the cyclobutanone ring by α -*N*-methyl-*N*-tosyl or α -methoxy substituents directs oxygen insertion regiospecifically toward the substituent. (198a) Similar attachment of an alkyl group (238) or even a halogen, (239) which in steroids often retards migration of the attached carbon, (240, 241) leads to formation of regioisomeric mixtures. A bridgehead will migrate in preference to a cyclopropyl, (238) or an α -carbon substituted by an alkyl and a halogen. (242) Several cyclobutanones fused to bridged rings react with basic hydrogen peroxide to give preferentially methylene migrated lactones, (243, 244)

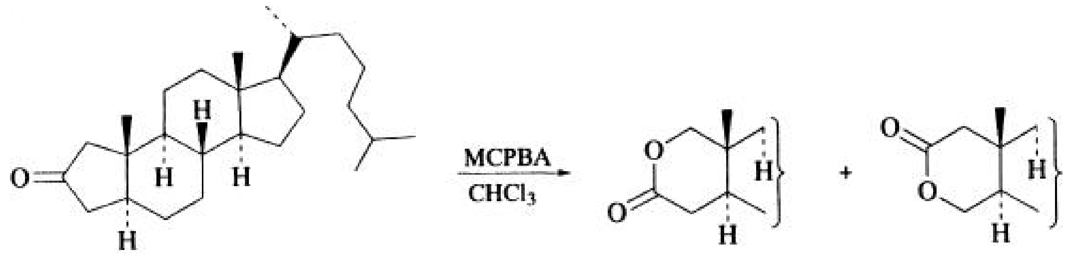
Cyclobutanone oxidations are integral reactions for syntheses of prostaglandins, (231, 233, 237, 245) lactone-annelated steroids, (246) α -methylene- γ -lactones, (226, 238) and paniculide A. (247, 248) The lactone ring of ginkolide B intermediate **72** is introduced in a regioselective and chemoselective fashion using basic triphenylmethyl hydroperoxide. (249, 250)



72 (86%)

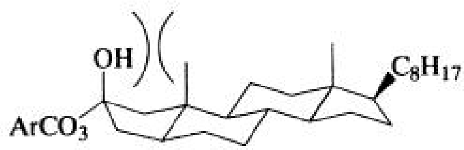
Fused-ring cyclopentanones in which the carbonyl is adjacent to a bridge position or an alkyl substituent react with organic peracids to give migration of the more substituted carbon. (251-253) Such oxidations are utilized as part of an approach to cyclohexenones (254) and in syntheses of the lactone moieties of the klaineanone ring system of quassinoids, (255, 256) xylomollin, (257) and lineatin. (258, 259) Lactone ring openings of substituted fused five-membered rings are involved in stereocontrolled syntheses of sesquifenchene and epi- β -santalene, (260) precapnelladiene, (261) damsin, (222, 262) alpinigenine, (263) sarracenin, (227) and thienamycin. (264)

If the carbonyl group in fused rings is flanked by two methylene groups, the preferred regioisomer upon oxidation in the absence of overriding electronic considerations results from movement of the bond which best relieves steric strain in the Criegee intermediate. This usually results in migration of the group nearest the more highly substituted carbon. (265) Thus, A-nor-2-keto-steroids prefer migration of C-1 (70–100%) (Eq. 12). (266-268) Attack of peracid on the less–hindered α face of the carbonyl



73 (80%) (20%)

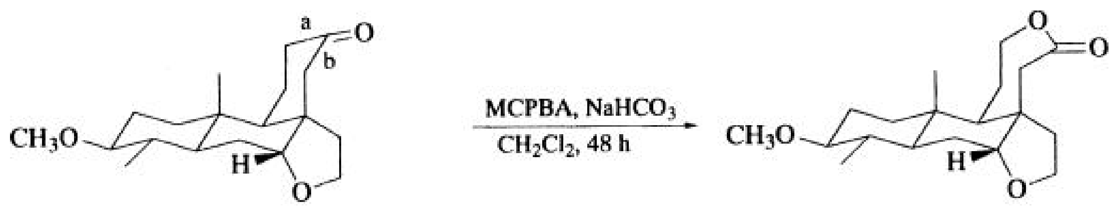
(12)



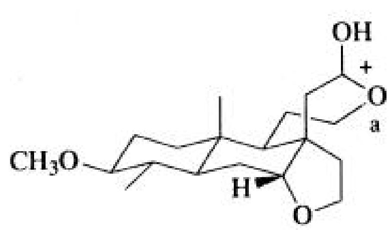
74

of **73** provides the Criegee intermediate **74**. Either C-1 or C-3 can orient *anti* to the peroxide bond, but there is greater relief of nonbonded interactions between the hydroxy and the bridgehead methyl when C-1 migrates. (267)

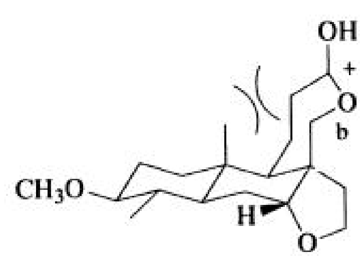
An exception in which the methylene group farthest from a tertiary bridgehead carbon migrates is the MCPBA oxidation of ketone **75** to give lactone **76**. (269, 270) The adverse 1,3-diaxial steric interaction between the C-12 methylene and the axial C-10 methyl group encountered upon migration of bond **b** to give **77** is absent in **78**, formed by migration of bond **a**.



75 76 (66%)



78

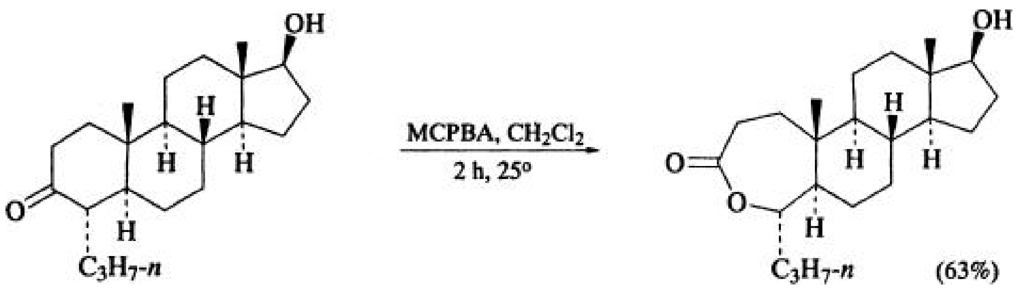


77

The Baeyer–Villiger cleavage of stereoselectively substituted fused six-membered rings, followed by lactone ring opening, results in a stereocontrolled route to side chains. Ring opening of lactone **79** is used in a synthesis of eriolangin and eriolanin, (223) other examples of this method include syntheses of glycinoeclepin A (271) and ivangulin. (272)

79 (81%)

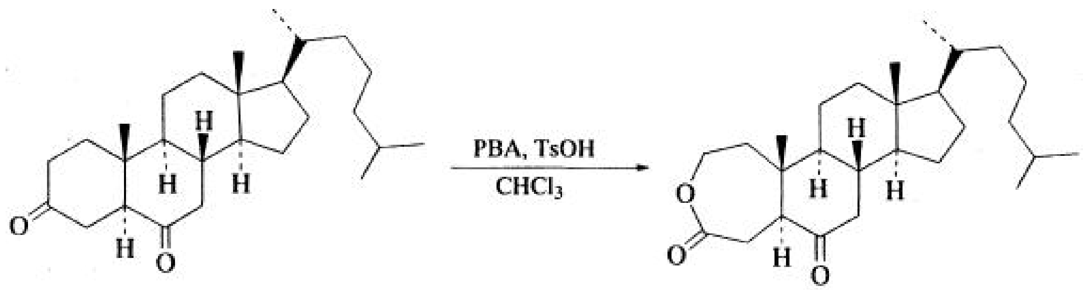
The Baeyer–Villiger procedure has been applied to steroids with carbonyl groups at all possible ring positions. If there are no heteroatom substituents on the steroid or if the heteroatom substituent is far removed, then the major product of oxidation is derived from migration of the more substituted ligand. With carbonyl groups at C-1, C-4, C-6, C-7, C-11, C-12, C-13, and C-17 this results in preferential insertion of oxygen at a bridgehead position. Single regioisomers are reported except for some C-6 (273) and C-17 (274) ketones. Although single regioisomers are often reported, careful study of ketones flanked only by methylene groups indicates mixtures with insertion of oxygen mainly toward C-1 (75%) for 2-ketosteroids and primarily (90%) toward C-17 for 16-ketosteroids. (267, 275) Although 3-ketosteroids show little regiochemical preference upon oxidation, (241, 275) an *n*-propyl group at C-4 is sufficient to impart total regioselectivity (Eq. 13). (276)



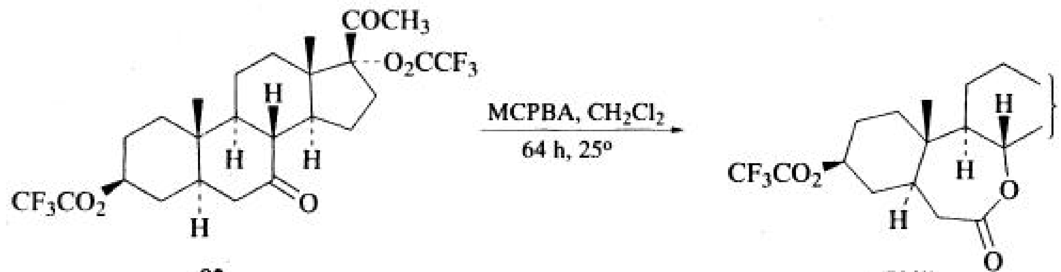
(13)

The normal preference for oxidation of cyclopropyl ketones is primary > cyclopropyl. (42, 45) However, the cyclocholestan-6-one **80** undergoes oxygen insertion next to the cyclopropyl group. (275, 277)

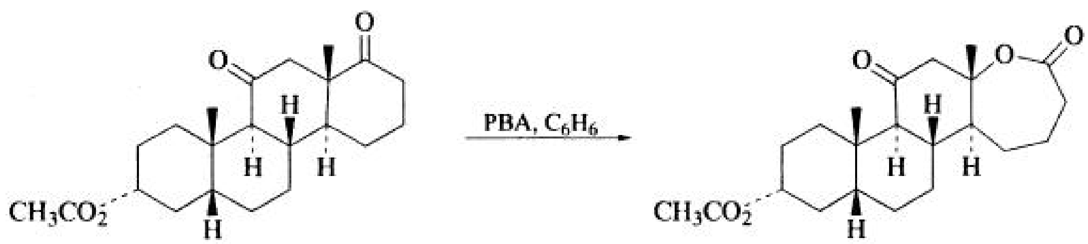
Cholestan-3-one has reactivity toward perbenzoic acid similar to that of cyclohexanone. (149) The rates of oxidation of steroidal ketones with perbenzoic acid show that a 3-ketosteroid reacts 30–80 times faster than a 17-ketosteroid, which reacts about twice as fast as a 20-ketosteroid. (149) Chemoselective oxidation of 5- α -cholestan-3,6-dione **81** introduces a single oxygen next to C-2. (278) The pregnan-7,20-dione **82**, a precursor of 7-oxaprogesterone, reacts only at the C-7 carbonyl, (279) and the D-homoetiocholan-11,17a-dione **83** reacts only at the C-17a. (280) A 3,17-diketo-4,5-dehydrosteroid



81 (63%)

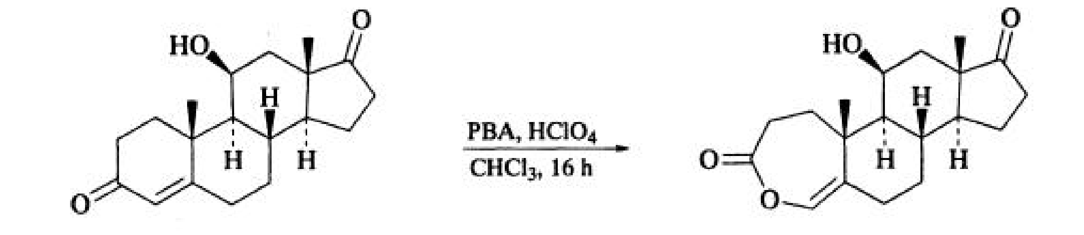


82 (70%)

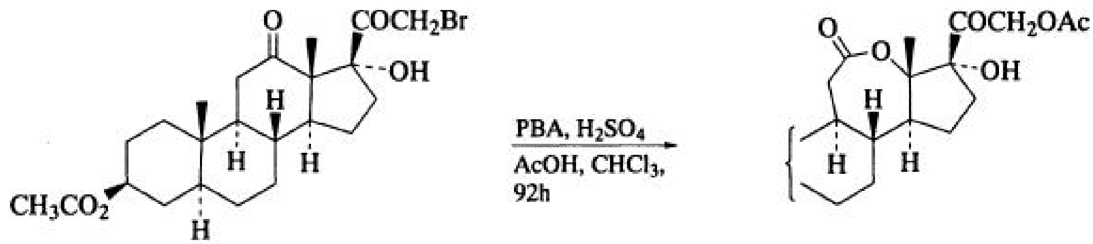


83 (85%)

84 reacts only at C-3 with perbenzoic acid, (281) and a 12,20-diketosteroid **85** reacts only at C-12. (282, 283)

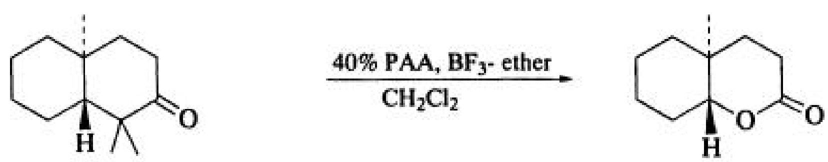


84 (60%)



85 (36%)

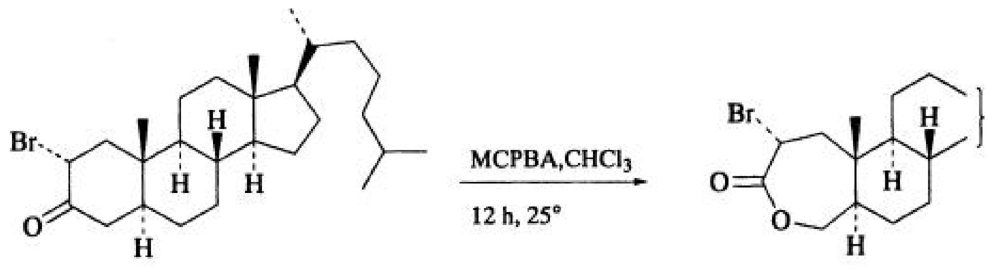
When a 4,4-dimethyl substituted 3-ketosteroid, or similar fused system, is treated with peracetic acid in the presence of boron trifluoride an exhaustive oxidation occurs (Eq. 14). (284) The method is useful since the lactone formed can be used to make conjugated ketones. (251, 284, 285)



(41%)

(14)

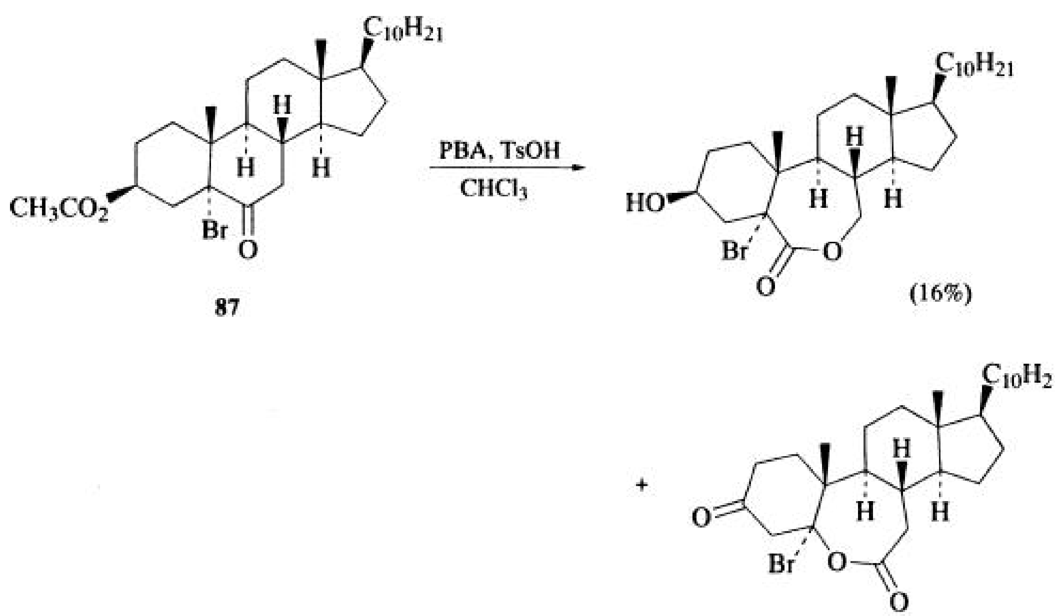
Heteroatom substituents at the α position to the carbonyl have a marked effect upon the regiochemical outcome of Baeyer–Villiger oxidations of fused ring systems. An α -bromine atom usually retards migration of the attached carbon; this effect, as shown with bromoketone **86**, is the basis of a method for preparing regioisomerically pure lactones from 3-ketosteroids. (240, 241, 266, 286) Insertion of oxygen



86

(97%)

adjacent to a bromine-containing bridgehead has been reported to 5- α -bromocholestan-6-one (287) and the stigmastan-6-one **87**. (288)

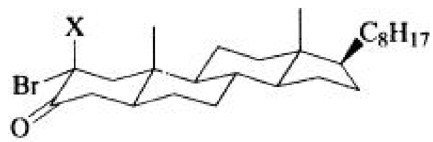


87

(16%)

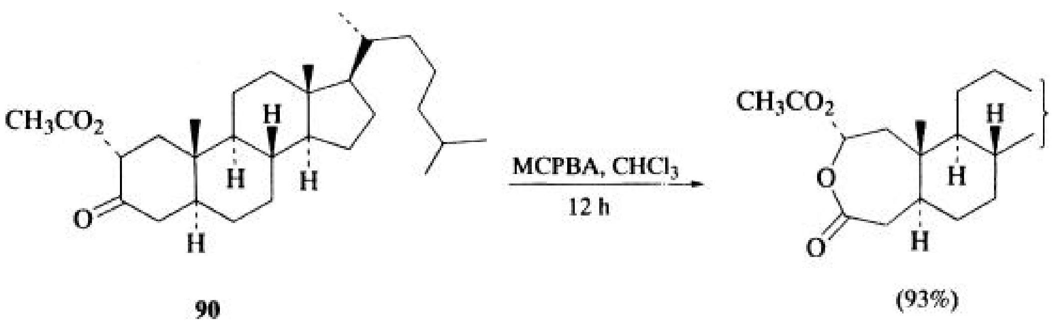
(47%)

Relative to cholestan-3-one, α -2-bromocholestan-3-one (**88**) reacts 13 times slower and 2,2-dibromocholestan-3-one (**89**) reacts two times faster. The equatorial α bromine in the plane of the carbonyl decreases the polarity of the carbonyl bond and hinders reaction, while the axial β bromine facilitates reaction, since orbital interaction stabilizes a positive charge at the adjacent carbonyl. (149)



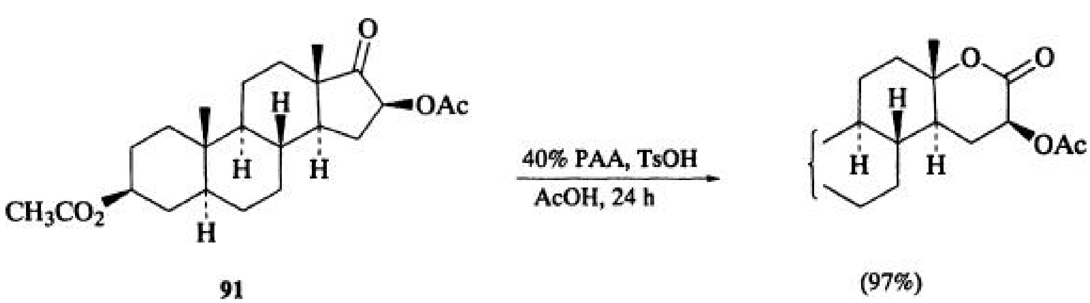
88 X = H
89 X = Br

An acetate ester α to the carbonyl in competition with a methylene group *generally* directs migration of the attached carbon, (289-291) as shown by the reaction of the 2-acetylcholestan-3-one (**90**). (199) An acetate-substituted carbon also migrates over a



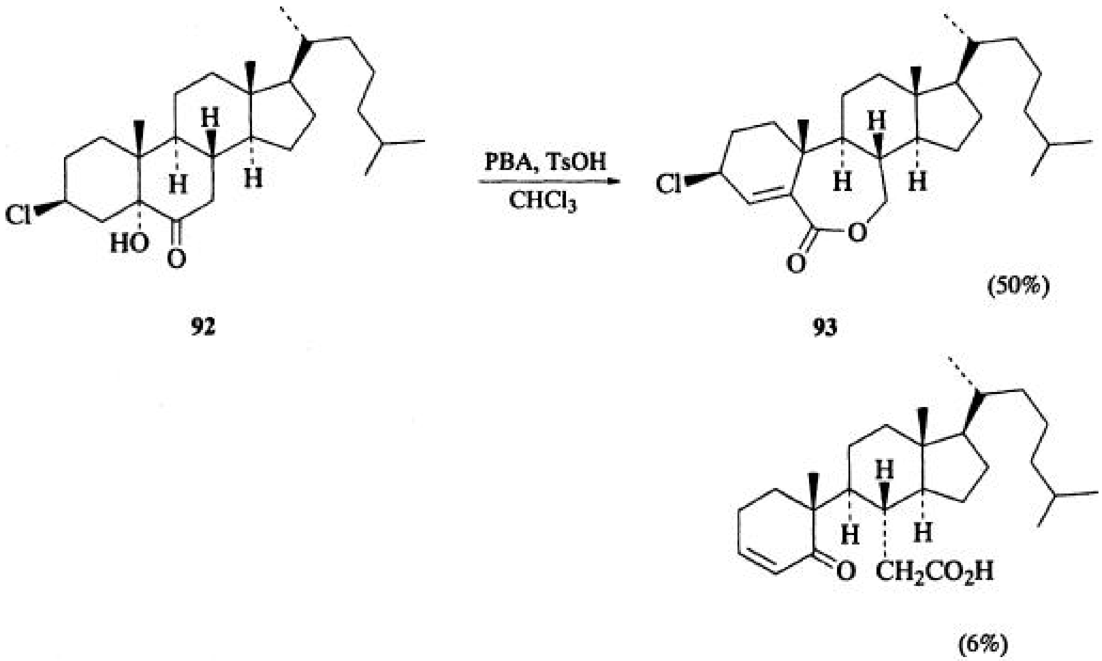
90

secondary bridgehead carbon. (292) A tertiary bridgehead carbon usually migrates in preference to a carbon attached to an acetoxy-substituted carbon as in the 16-acetoxyandrostanone **91**. (293, 294)



91

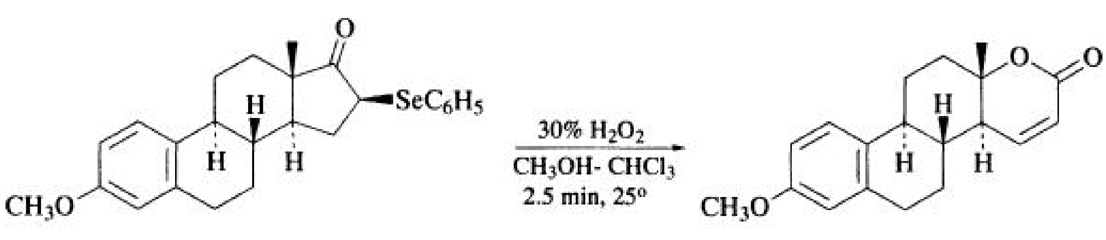
Migratory preferences with α hydroxy groups present are difficult to predict. A bridgehead 5- α -hydroxy group facilitates migration in a 3-acetoxy-6-ketosteroid, (295, 296) but not in the oxidation of 3-chloro-5- α -hydroxycholestan-6-one (**92**), in which a methylene-migrated lactone **93** is the major isolated product. (288) Migration of a secondary carbon rather than a hydroxy-substituted carbon has been reported. (266)



92 93

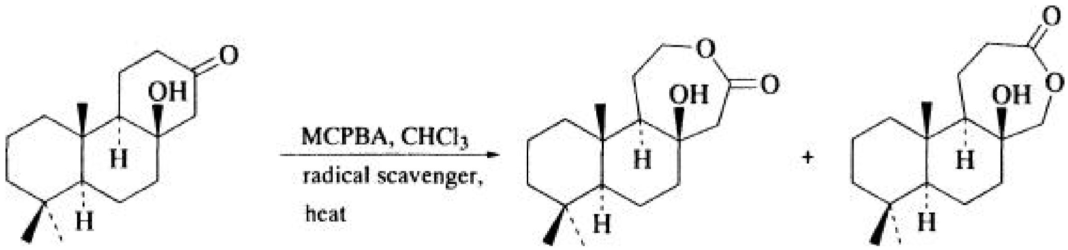
An α ether in the form of an epoxide normally facilitates migration; (297, 298) however, when basic hydrogen peroxide is used as oxidant, C-1 migrates in a 2-keto-3,4-oxido-A-norsteroid. (299) Regioselective migrations occur when both adjacent methylenes have ether or ketal oxygen substituents; however, no clear pattern to predict migration has emerged. (300, 301)

C-16- α -Phenylseleno ketones, such as **94**, (109) undergo rapid Baeyer–Villiger oxidation with regioselective bridgehead migration and selenoxide elimination when treated with 30% hydrogen peroxide. The active oxidizing agent is probably a peroxyseleninic acid generated in situ. (302)

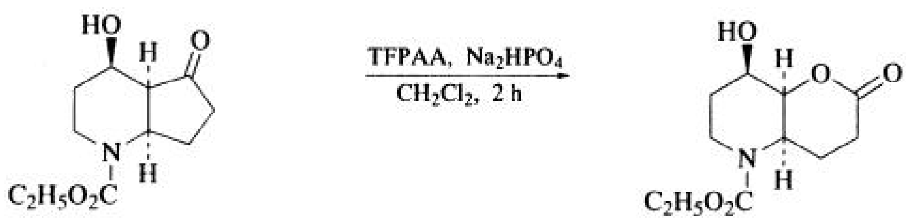


94 (66%)

A ketal oxygen at position C-5 of a 3-ketosteroid directs migration away from the proximal methylene, (303) but the β -hydroxy ketone **95** gives migration of both methylene groups. (304, 305) The β -hydroxy and β -*N*-acyl substituents of ketone **96** do not block favored migration of the secondary bridgehead position. (85)

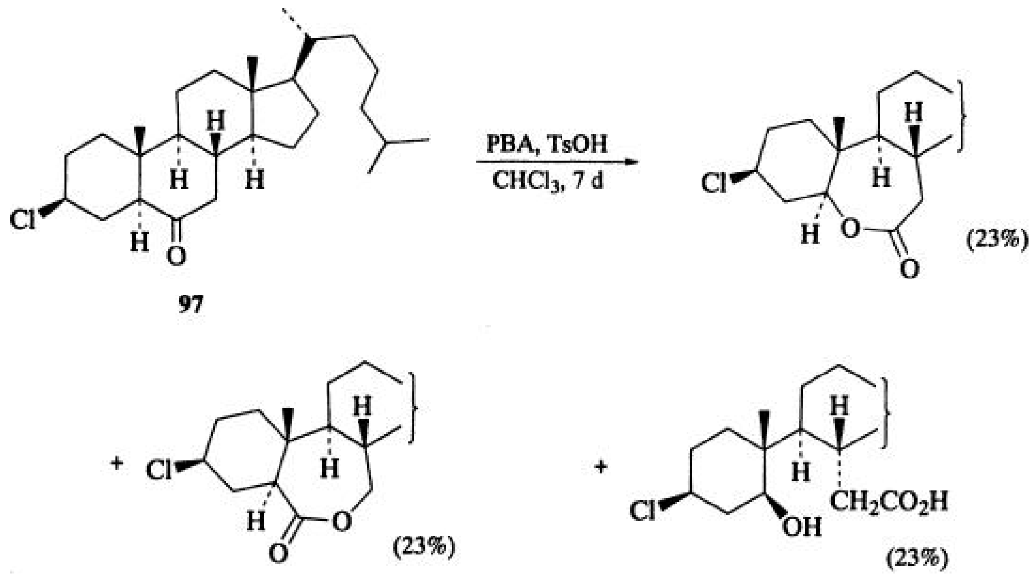


95 (34%) (49%)

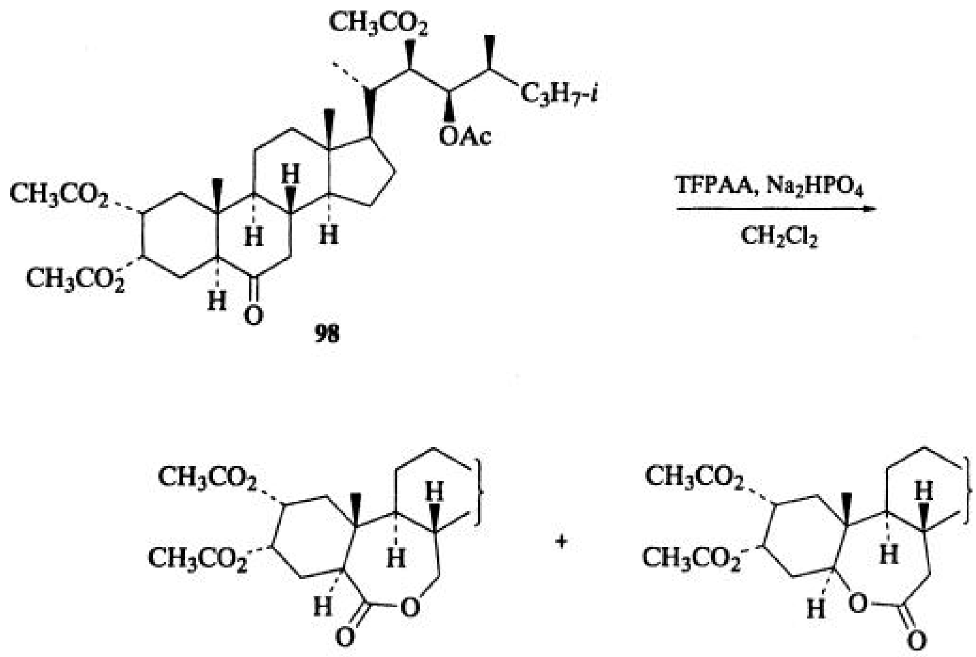


96 (50%)

The tendency for bridgehead migration in 6-ketosteroids is reduced by electron-withdrawing γ -halogen, (277, 306-308) hydroxy, (306) or acetoxy (273, 306, 309, 310) substituents at C-3. (287, 303) The γ -chloroketone **97** affords a mixture of products from both bridgehead and methylene migration. (306) Electron withdrawal by 3-halo, 3-acyloxy, or 3-hydroxy substituents sometimes reduces the rate of MCPBA oxidation of 6-ketocholesterols. Relative to 6-ketocholesterol, a 3- α -chloro, 3- β -hydroxy, 3- β -acetate, or 3- β -bromo substituent cuts reaction rate in half while 3- β -chloro or 3- β -2,2-dimethylpropionate groups have neglible rate effects. (311)



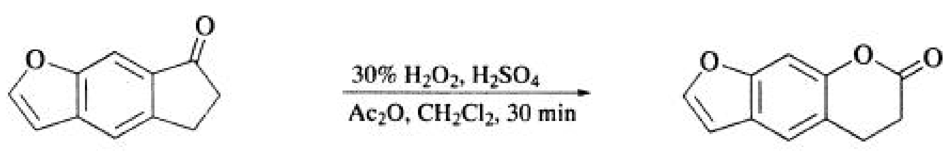
A systematic study of the effects of remote β , γ , and δ oxygen containing substituents on the regiochemistry of buffered TFPAA oxidations of 5- α -cholestan-6-one derivatives showed a minor percentage of migration of the C-5 bridgehead in all cases. (273) Since methylene migration dominates, the naturally occurring lactone brassinolide (**99**), a plant growth promoter, can be prepared from ketone **98**. (312, 313) The regiochemistry of migration is catalyst dependent, since bridgehead migration to give lactone **100** is preferred if the oxidation of **98** is performed with TFPAA in methylene chloride with 1% sulfuric acid/10% acetic acid. (314)



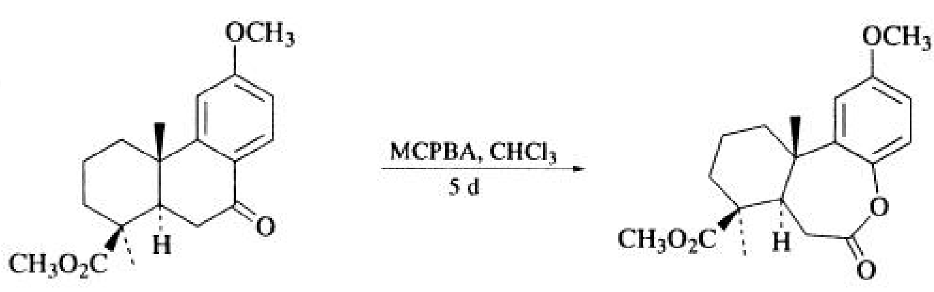
99 (71%) **100** (7%)

3.3.1.2. Oxidation of Benz-Fused Ketones

Psoralen (**102**) can be prepared from benz-fused ketone **101** by a regioselective migration of the aryl group over a primary methylene. (315) The Baeyer–Villiger procedure can be used to introduce an oxygen functionality at C-11 of structures similar to ketone **103** by ring opening of the derived lactone **104**, rotation, and Friedel–Crafts acylation at the original C-11. (116)

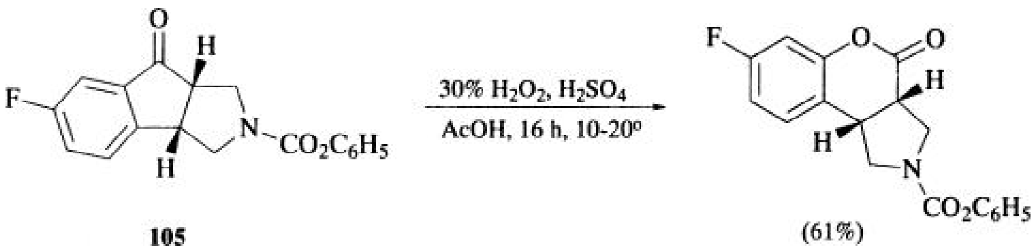


101 **102** (71%)



103 **104** (88%)

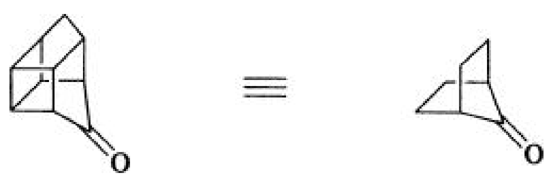
Preferential migration of an aryl ring is also generally preferred over a secondary carbon. Aryl migration is aided by an electron-donating *o*- or *p*-acetate on the ring. (316) The ring fluorine does not deter aryl migration in ketone **105**, in which alkyl migration may be deterred by the β-carbamate substituent. (317) An example of preferential secondary-alkyl migration is reported, but in extremely low yield. (318) If a ketone is di-benz-fused, the preferential migrating group is the more electron-releasing one. (2, 319, 320)



105

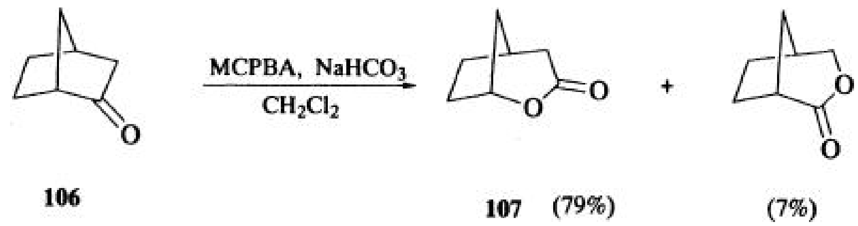
3.4. Reactions of Bridged Bicyclic and Polycyclic Ketones

The ketones in this section, irrespective of unsaturation or heteroatom substitution, are organized according to the structure of the parent bridged hydrocarbon. For polycyclic ketones, the ring system is considered to be the bridged bicyclanone with the smallest sum for the three bridging units, and the ring system is numbered arbitrarily as this bicyclic ketone would be numbered.



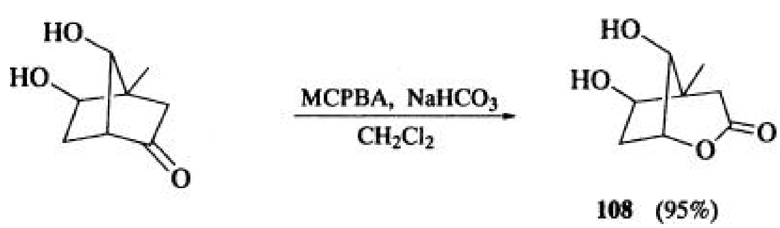
3.4.1.1. Oxidation of Bicyclo[2.2.1]heptanones

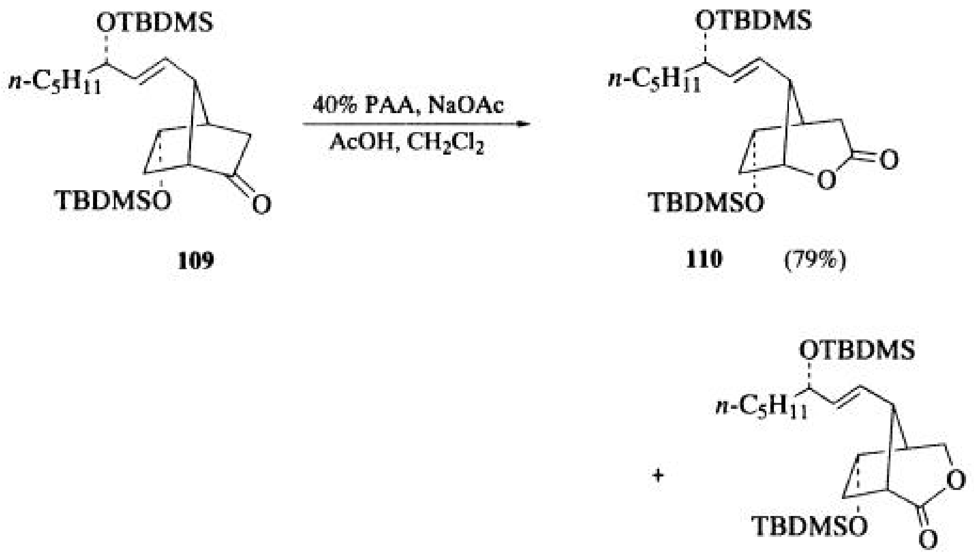
Baeyer–Villiger oxidation of norbornan-2-one (**106**), which is available in chiral form, (321) provides mainly the bridgehead migrated lactone **107**. (322, 323) This lactone serves as a rigid template for further functionalization reactions, and is used in stereocontrolled syntheses of the cinchona, (324, 325) yohimbane, (325) emetine, (326, 327) and coryanthe-type alkaloids. (328)



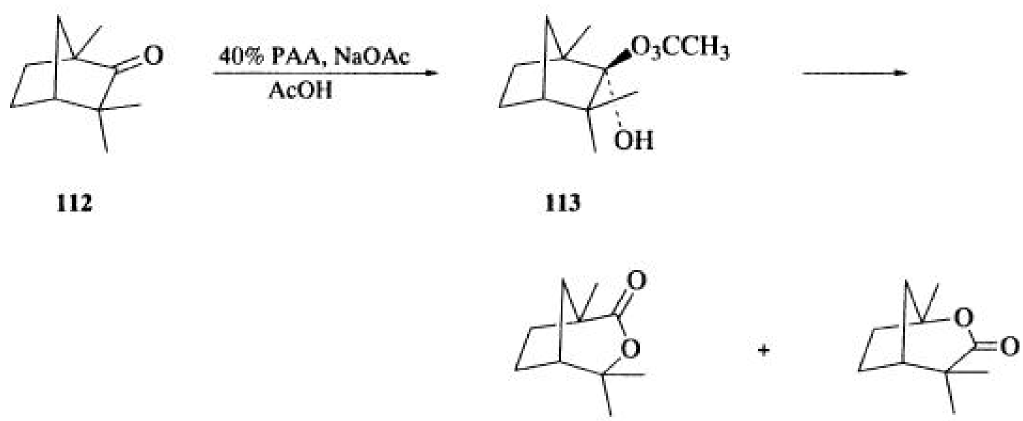
Substituted norbornan-2-ones provide access to polyfunctional cyclopentanol derivatives; lactone **108** is an intermediate in the synthesis of verrucarol. (329-331) Oxidation of the prostaglandin precursor **109** provides a mixture of regioisomeric lactones **110** and **111**. (332, 333) The minor methylene-migrated lactone **111** can be removed by preferential hydrolysis with dilute aqueous base. (334, 335) In addition to extensive use in prostaglandin syntheses, (332, 333, 336-353) substituted norbornan-2-ones are precursors of (–)-terrecyclic acid **A**, (354) boschniolactone, (355) triquinacine, (334) a 19-norsteroid, (356) spatane diterpenes, (357) and methyl dihydrojasmonate. (358, 359)

The preference for bridgehead migration in the oxidation of norbornan-7-ones can be altered by substitution at C-3 and C-7. (9) A single methyl group at C-3 results in a 1:1 mixture of bridgehead and nonbridgehead migrated lactones; (360) the formation of mainly lactone **114** from fenchone (**112**) has been attributed to greater relief of eclipsing interactions in the Criegee intermediate **113** for movement of C-3. (361, 362)



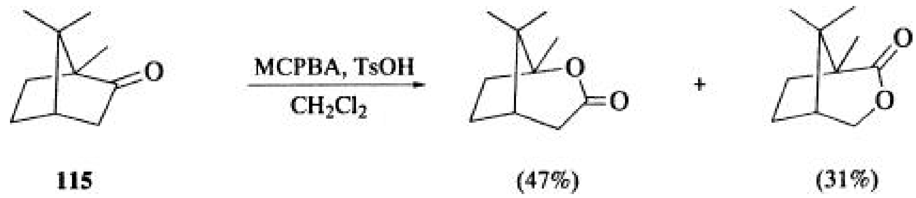


109 **110** (79%) **111** (21%)



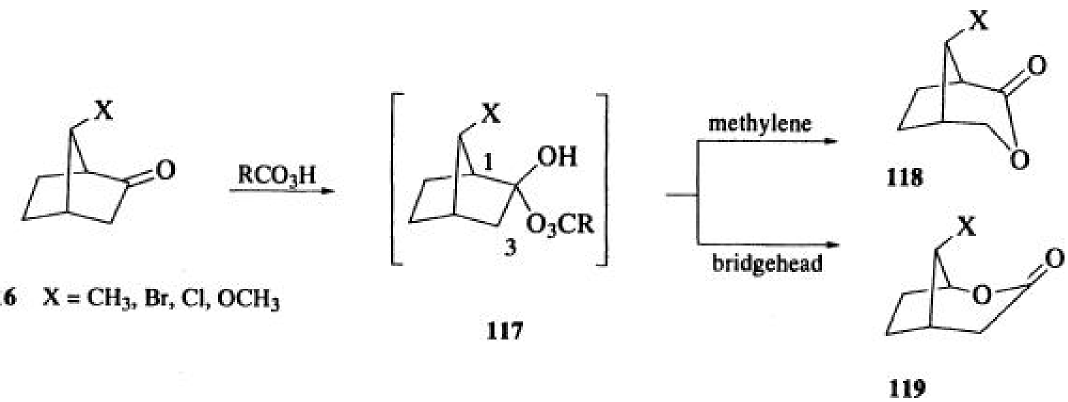
112 **113** **114** (21%) (14%)

Bridgehead migration is favored upon oxidation of 1-methylbicyclo[2.2.1]heptan-2-one. (323, 362) Oxidation of camphor (**115**) also gives preferred C-1 migration. (362-364) However, in those cases where stereochemistry has been unambiguously defined (365) and the bridgehead C-1 is unsubstituted, (362, 363, 366) oxidation of a 7-*syn*-methyl-, (362, 367, 368) 7-*syn*-halogen-, (361, 369) or 7-*syn*-methoxy-substituted norbornan-2-one (**116**) (369) results in preferential methylene migration. An argument that has been



115

advanced to explain this phenomenon assumes that the 7-*syn* substituent blocks attack of the peracid from the *exo* direction and gives rise to the Criegee intermediate **117**. Migration of the C-3 methylene carbon involves a lower energy transition state proceeding through a chair-like conformation to give **118**, while migration of the C-1 bridgehead carbon proceeds through a less favored boat-like conformation to **119**. (361, 362, 370, 371) In support of this suggestion, if a 7-*syn* substituent facilitates addition of peracid to the *exo* face by hydrogen bonding or other interaction, (358) bridgehead migration is preferred. Accordingly, with MCPBA and a 7-*syn*-carboxylic acid (100%), (371a) 7-*syn*-methoxycarbonyl (95%), (358, 369) 7-*syn*-hydroxymethyl (100%), (371b) 7-*syn*-acetate (60%), (369) or 7-*syn*-*p*-toluenesulfonyl (369) (62%) group, bridgehead migration dominates.

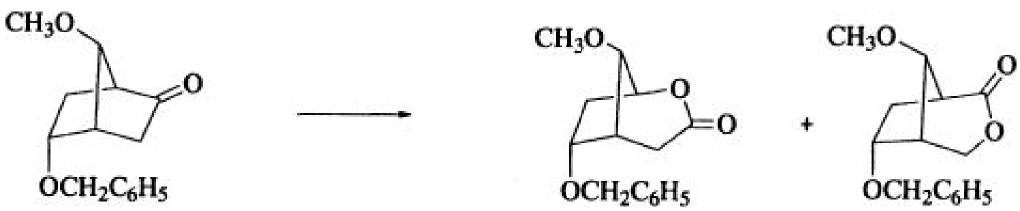


116 X = CH_3, Br, Cl, OCH_3

Norbornan-2-ones with *tert*-amino, (347-371c) acetate, (369) methoxy, (369) or carbomethoxy (369) substituents in the 7-*anti* position, which is beta to the migrating bridgehead and sterically remote from the C-2 carbonyl, undergo bridgehead migration during oxidation. As the electron-withdrawing power of the 7-*anti* substituent increases, (371c) the propensity for bridgehead migration decreases; for example, 7-*anti*-cyano (0% bridgehead) (349) and 7-*anti*-*p*-toluenesulfonyl (60% bridgehead). (369) A second substituent at C-5-*endo* also has an influence on the regiochemical outcome. (371c) Oxidation of 5-*endo*-acetoxy-7-*anti*-methoxynorbornan-2-one with performic acid gives 70% bridgehead:30% methylene migration. (349)

The choice of peracid and solvent influences regiochemistry in the oxidation of

5-*endo*-benzyloxy-7-*anti*-methoxynorbornan-2-one (**120**) (Table 4). (349) The selectivity for bridgehead migration is greatest with peracetic acid in the weakly acidic acetic acid solvent. Preference for migration of the more electron-donating bridgehead carbon, which can better stabilize the transition state for loss of acetic acid during



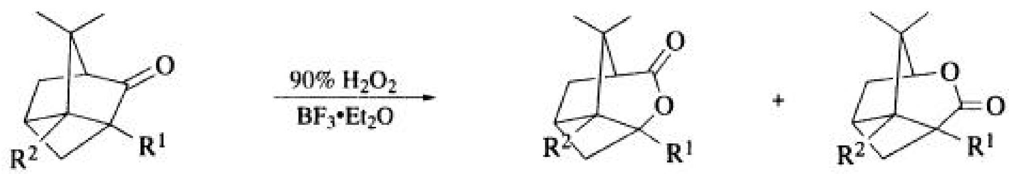
120 121 122

decomposition of the reactive Criegee intermediate, assumes greater importance with a poor leaving group.

Table 4. The Effect of Peracid on the Regioselectivity of the Baeyer–Villiger Reaction of Norbornan-2-one 120 (349)

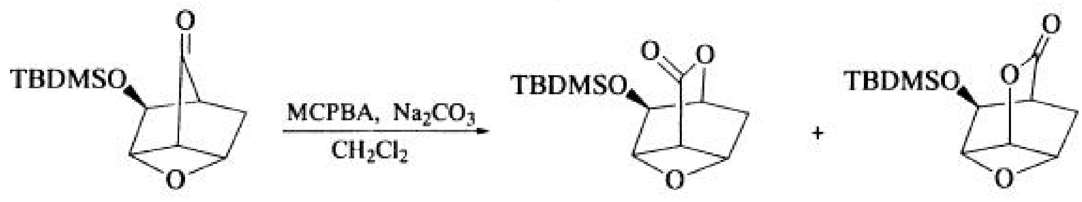
Peracid	Solvent	Ratio (121:122)
MCPBA	CH_2Cl_2	55:45
Permaleic	CH_2Cl_2	67:33
Perphthalic	$CHCl_3$	73:27
Performic	HCO_2H	85:15
Peracetic	CH_3CO_2H	92:8

The 2-methyl-2,6-methylene-bridged norbornan-2-one **123** inserts oxygen only at the tertiary cyclobutyl carbon to give lactone **124**; an unspecified mixture of regioisomers forms from **125** when the methyl is not adjacent to the carbonyl. (372) The bridged norbornan-7-one **126** undergoes regioselective oxidation to lactone **127**. (373) The electronegative oxetane retards migration. If the 2,6 position of a 7-norbornanone is bridged by a methylene instead of an oxygen, only migration of the cyclobutyl ring occurs. (374) Migration of a secondary bridgehead carbon is preferred over a bridgehead cyclopropyl carbon in the oxidation of the bridged norbornan-2-ones **128**. (340, 343, 375, 376)

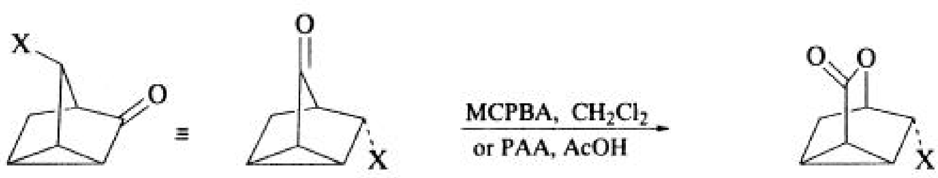


123 $R^1 = CH_3$, $R^2 = H$ ⟶ (76%) **124**

125 $R^1 = H$, $R^2 = CH_3$ ⟶ (56%) mixture of both lactones

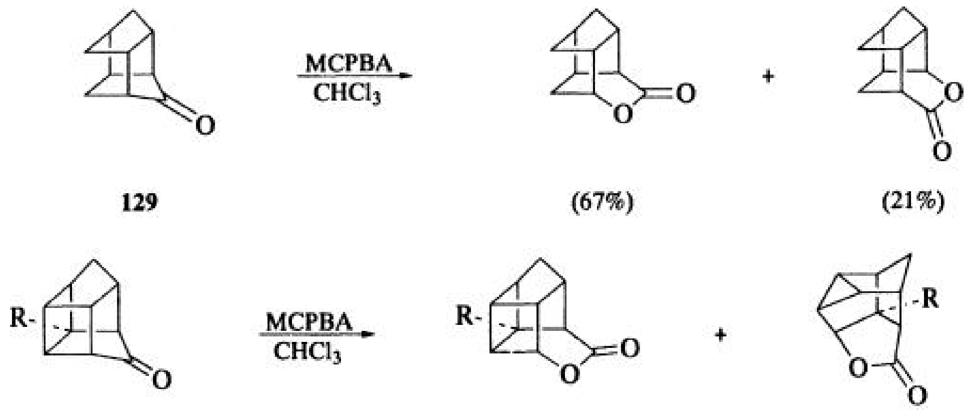


126 **127** (83%) (9%)



128 X = H, CO_2CH_3, CO_2H (56-100%)

The caged structures **129** and 1,4-bis-homocubanone (**130**) are formally bicyclo[2.2.1]heptan-7-one derivatives. (377, 378) Oxidations of related bis-homocubanones with peracetic acid or MCPBA generally insert oxygen preferentially toward the cyclobutane ring, (377-380) although regioisomeric mixtures are reported. (378) Oxidations of caged ketones are often accompanied by rearrangement (Eq. 15). (377, 379) Conversion of the caged structure homopentaprismanone to pentaprismane involves a Baeyer–Villiger oxidation. (381)



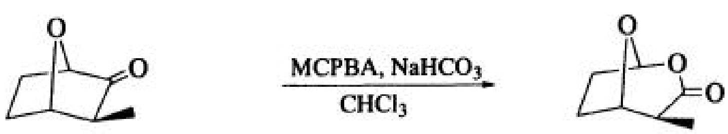
129 (67%) (21%)

(15)

130 (54%) (16%)

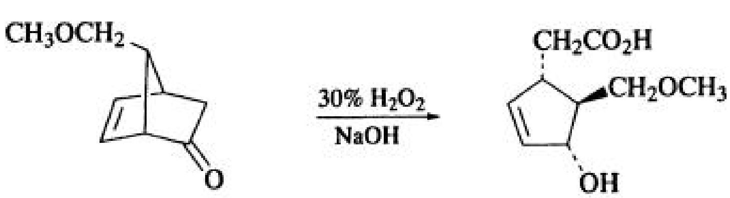
R = $CO_2CH_2C_6H_4NO_2$-*p*

The α -oxygen atom of 7-oxanorbornan-2-one (**131**), in competition with a secondary carbon, directs migration toward the bridgehead. (382-386) Lactone **132** is a precursor of methyl nonactate, (382, 383) and lactones derived by oxidation of 5,6-substituted-7-oxanorbornanones are used to prepare carbohydrates (382, 385-388) and alkaloids. 388a–e



131 **132** (94%)

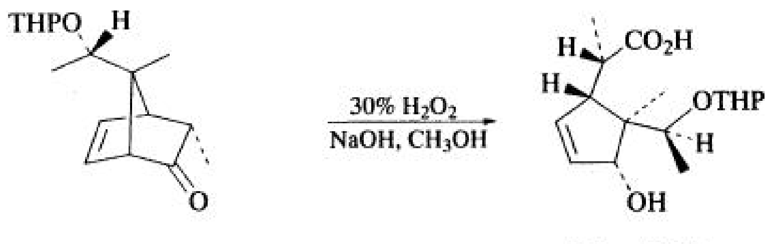
The lactone formed upon oxidation of norbornen-2-one has been used to prepare the cyclopentane ring of brefeldin-A, (389) and substituted norbornen-2-ones have found extensive use in the synthesis of prostaglandins (337, 344, 390-411) and prostacyclins. (412) Chemospecific oxidations with regiospecific bridgehead migration occur with basic 30% hydrogen peroxide (Eq. 16). (390) The preference for migration of the



(99%)

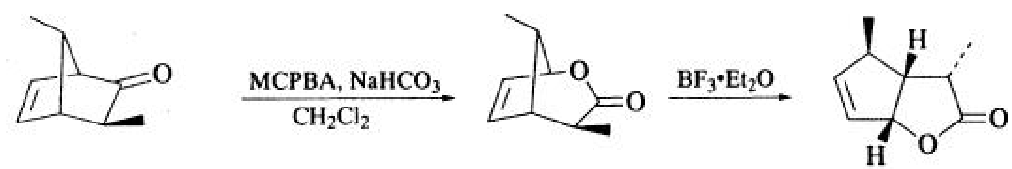
(16)

allylic bridgehead is unaffected by substitution of a 7-*syn* methyl group (60, 262, 405, 413-415) or by 3-methyl groups. (60, 405, 414-416) The hydroxyacid **134** formed upon oxidation of ketone **133** has been utilized in the synthesis of pseudoguaianolides, (405, 414, 415) and similar structures modified at C-7-*anti* and C-3 have been utilized to prepare a helenanolide (405) and estrone. (413)



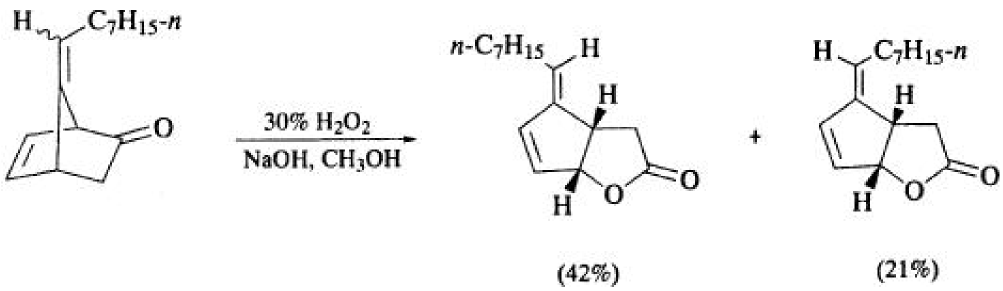
133 **134** (75%)

If the lactone or hydroxy acid derived from a norbornen-2-one is treated with a Lewis acid in an aprotic solvent, an isomeric fused-ring lactone derived by allylic alcohol rearrangement is formed (Eq. 17). (417) This rearrangement has been used to

 (17)

135 (84%)

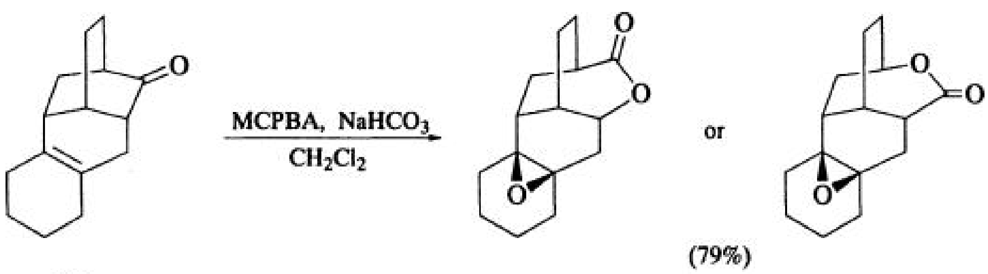
synthesize lactone **135**, a precursor of the Prelog–Djerassi lactone, (416) and to prepare lactones used in the synthesis of a sterol D-ring and side chain, (413, 414) thienamycin, (418) and the Inhoffen-Lythgoe diol. (60) Oxidation of 7-alkenylnorbornenones gives only epoxidation with MCPBA, but provides allylically rearranged lactones with basic hydrogen peroxide (Eq. 18). (409)



(18)

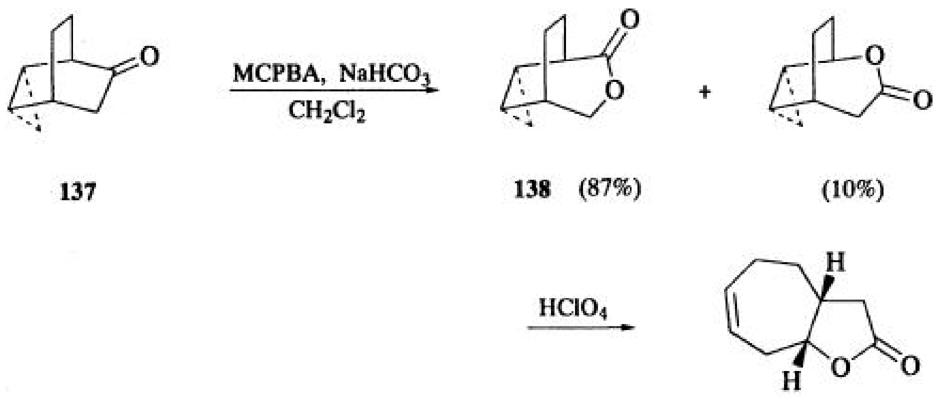
3.4.1.2. Oxidation of Bicyclo[2.2.2]octanones

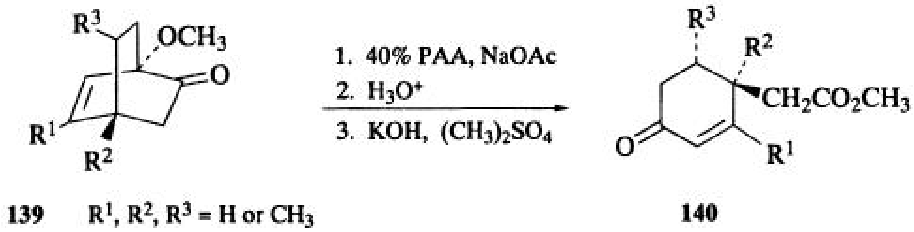
Baeyer–Villiger oxidation of bicyclo[2.2.2]octan-2-ones unsubstituted on the C-3 methylene carbon gives solely bridgehead migration. (371, 419, 420) MCPBA oxidation of ketone **136**, which has two secondary alkyl substituents, nevertheless provides a single unidentified lactone regioisomer. (421) Unlike the *syn*-cyclopropyl isomer in the norbornan-2-one series,



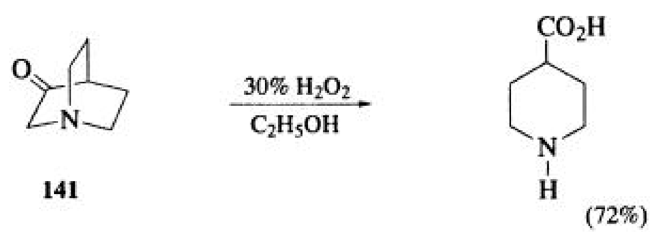
136

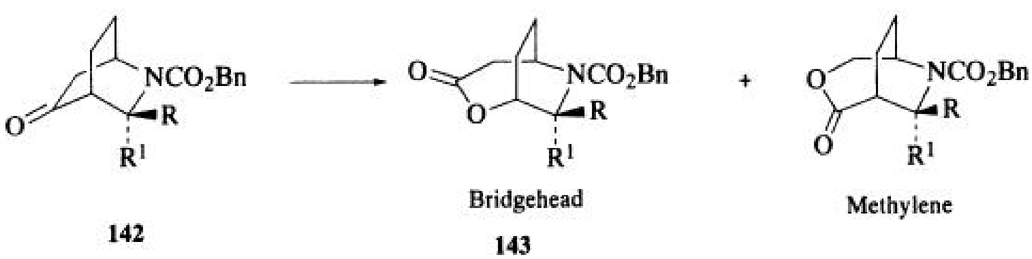
which has an 80:20 preference for bridgehead migration, oxidation of the *syn*-cyclopropyl ketone **137** results in major methylene migration to give **138**. The *anti*-cyclopropyl isomer of **137** and *anti*-cyclopropyl homolog in the norbornan-2-one series give only bridgehead migration. (422) Oxidation of 1-methoxybicyclo[2.2.2]octenones **139** with bridgehead migration and lactone ring opening provides 4,4-disubstituted cyclohexenones **140**. (423)



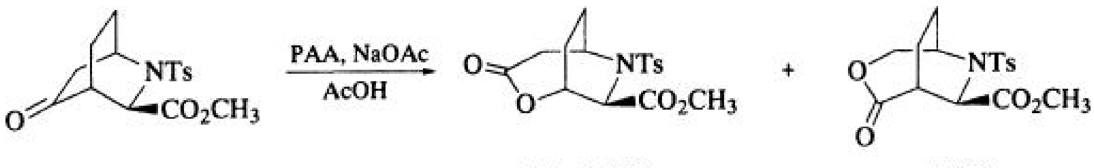


The bridgehead nitrogen atom facilitates cleavage of 1-azabicyclo[2.2.2]octan-3-one (**141**) between the carbonyl and adjacent methylene group. (73) The effect of substituent and peracid upon the regiochemistry of migration of 3-substituted 2-azabicyclo[2.2.2]octan-5-ones **142** is shown in Table 5. (424-426) Peracetic acid is more regioselective for bridgehead migrated lactones **143** than is MCPBA. Peracetic





acid oxidation of *N*-tosyl ketone **144** provides lactone **145**, a precursor of isoprosopinine B. (427)



144 **145** (45%) (12%)

Table 5. Effects of 3-Substituents on the Regiochemistry of Oxygen Insertion of *N*-Carbobenzoxy-2-azabicyclo[2.2.2]octan-5-ones 142 (424)

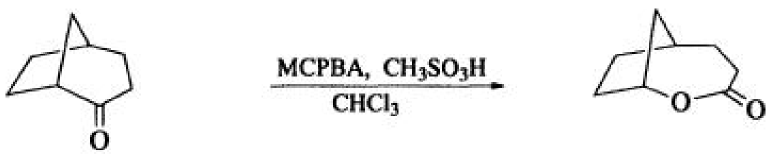
R	R[1]	Peracid[a]	BH Migration (% of 143)[b]	Yield (%)
H	H	PAA	100	90
		TFPAA	100	61
		MCPBA	69	89
		PNPBA[c]	67	78
H	CH_3	PAA	62	71
		MCPBA	50	85
H	C_6H_5	PAA	100	74
		MCPBA	60	83
H	$CH_2O_2CC_6H_5$	PAA	84	16
H	CO_2CH_3	PAA	100	60
		MCPBA	18	70
CH_3	H	PAA		0
		MCPBA	81	71

CO_2CH_3 H	PAA	66	57
	MCPBA	38	91

[a]PAA = 40% PAA/AcOH, NaOAc; MCPBA and PNPBA in CH_2Cl_2, $NaHCO_3$; TFPAA = 89% TFPAA, Na_2HPO_4, CH_2Cl_2.
[b]BH = bridgehead migrated lactone.
[c]PNPBA = *p*-nitroperbenzoic acid.

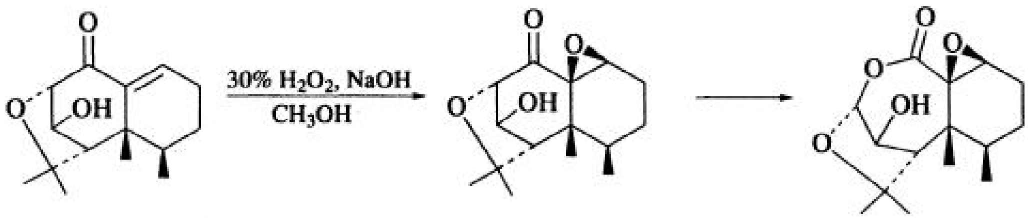
3.4.1.3. Oxidation of Bicyclo[3.2.1]octanones

Oxidation of bicyclo[3.2.1]octan-2-ones with PAA (428, 429) or MCPBA gives mainly bridgehead migration; (430) lactone **146**

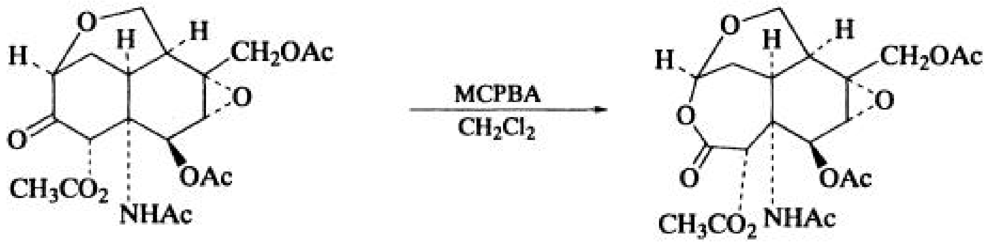


146 (80-90%)

was utilized in the synthesis of peristylane. (431) Regioselective bridgehead oxygen insertion is observed upon oxidation of 8-oxabicyclo[3.2.1]octan-2-ones, which have a ketal oxygen at C-3. (301) An α -ether oxygen adjacent to the bridgehead directs exclusive bridgehead migration for 7-oxabicyclo[3.2.1]octan-2-ones **147** and **148** in competition with 3-alkenyl (3- α -epoxide) or 3-acetoxy substituents. (432, 433)

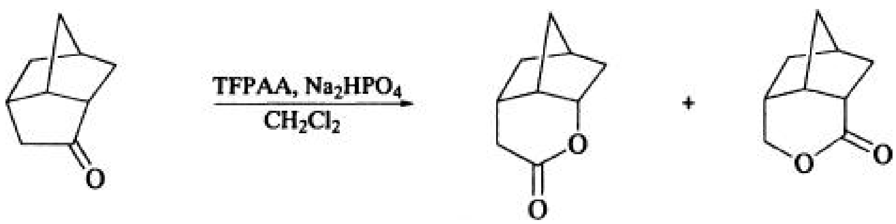


147 (43%) (—)



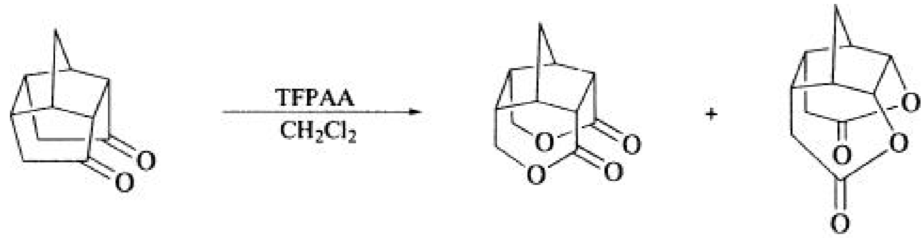
148 (100%)

Bicyclo[3.2.1]octan-6-ones normally oxidize with regioselective bridgehead migration. (434-436) However, oxidation of brendanone (**149**), a bridged bicyclo[3.2.1]-octan-6-one, provides a mixture of lactones with TFPAA, (437) and the tetracyclic

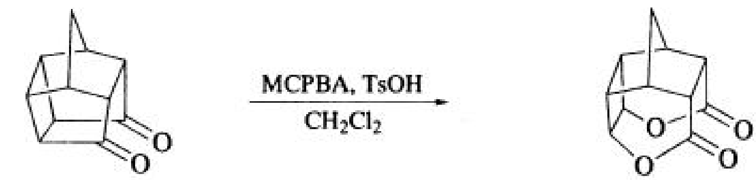


149 (46%) (38%)

ketone **150** gives nearly totally dimethylene migrated lactone **151**. (438) The related pentacyclic ketone **152** prefers cyclobutyl–carbon migration. (439, 440) Major migration occurs away from the bridgehead if a C-7- α -methyl is introduced onto a bicyclo[3.2.1]octan-6-one; (436)

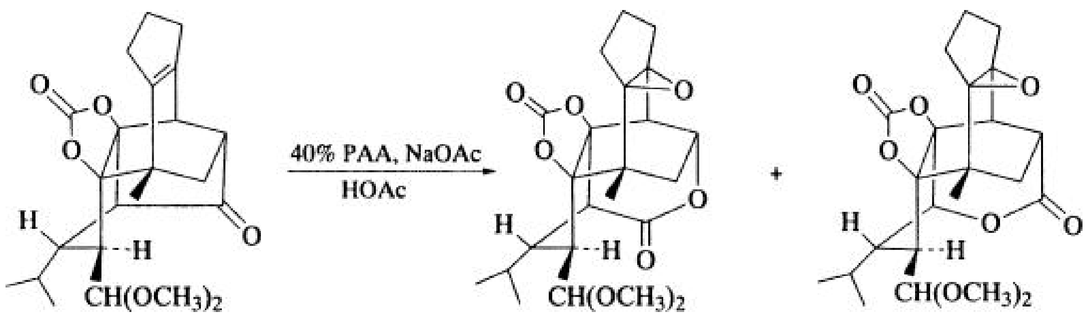


150 **151** (>71%) (<4%)



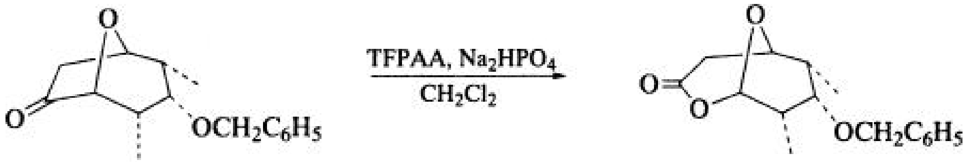
152 (81%)

however, the polycyclic ketone **153** provides mainly the epoxylactone **154**, an intermediate in a synthesis of ryanodol. (441)



153 **154** (69%) (12%)

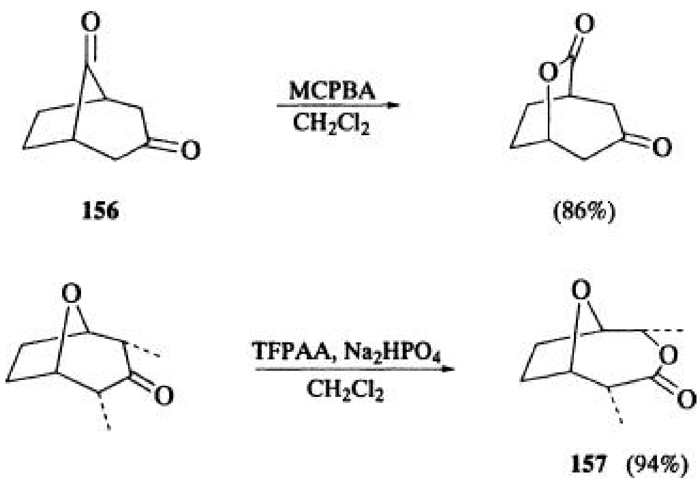
Bridgehead migration is favored by an oxygen atom adjacent to the bridgehead, and 8-oxabicyclo[3.2.1]octan-6-ones undergo regioselective bridgehead insertion of oxygen (Eq. 19). (442) Lactone **155** was used to prepare the C_{21}–C_{27} segment of rifamycin S. (443)



(19)

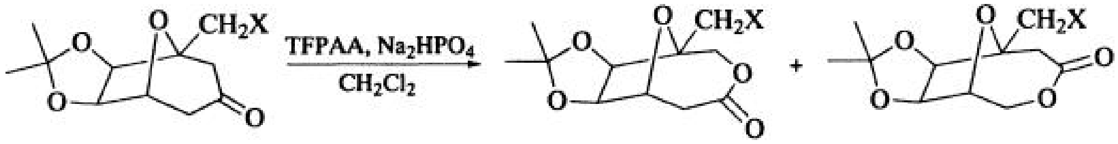
155 (80%)

Oxidation of bicyclo[3.2.1]octan-3-one with MCPBA (56 hours, 25°) is slow, (444, 445) and bicyclo[3.2.1]octa-3,8-dione (**156**) reacts only at C-8 with MCPBA. (444) Oxidation of an 8-*N*-methoxycarbonyl analog with MCPBA is successful under forcing conditions after 22 hours at 55° in the presence of the radical inhibitor 2,4,6-tri(*tert*-butyl)phenol. (446) The 3-carbonyl group of 8-oxabicyclo[3.2.1]octan-3-ones is oxidized without difficulty (Eq. 20). Lactone **157** is converted to nonactic acid. (447)



(20)

The Baeyer–Villiger oxidation of 8-oxabicyclo[3.2.1]octan-3-ones is used in the synthesis of *C*-nucleosides. (38, 448-463) The electronic effects exerted by remote γ substituents upon the regiochemistry of oxidations of ketones **158** and **159** is shown in Table 6. An increase in electron-withdrawing ability of the γ group X



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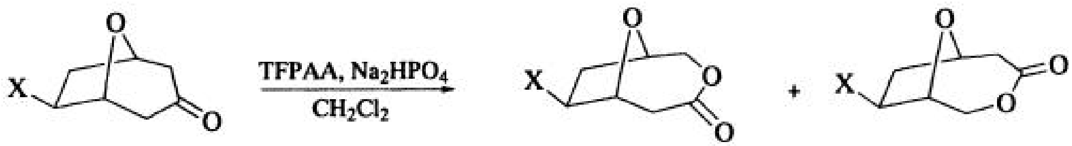

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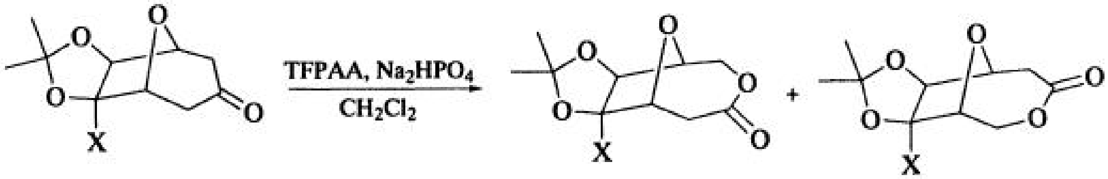

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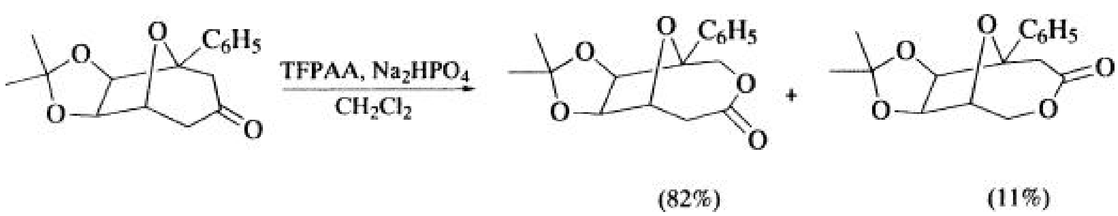
results in a decreased tendency of the nearest α carbon to migrate to an electron-deficient center of a Criegee intermediate. (9, 38, 39) With a C-1 phenyl group oxidation is highly regioselective for migration of the α -methylene group (Eq. 21). (38)



(21)

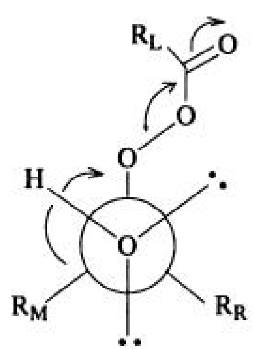
Table 6. Effects of γ Substituents on the Regioselectivity of Oxidation with 8-Oxabicyclo[3.2.1]nonan-3-ones 158–160 with TFPAA (9, 38)

Ketone (X Position)	γ -Substituent X	α -migration (%)
158 C-1′	$OSi(CH_3)_2C_4H_9$-*t*	55
	H	53

	C_4H_9-*n*	50
	$OCH_2C_6H_5$	48
	O_2CCH_3	35
	$O_2CC_4H_9$-*t*	31
	$O_2CC_6H_5$	28
	O_2CCF_3	23
	OSO_2CH_3	19
	OSO_2CF_3	14
159 C-6-*exo*	$OSi(CH_3)_2C_4H_9$-*t*	30
	$OCH_2C_6H_5$	30
	O_2CCH_3	46
	$O_2CC_4H_9$-*t*	35
	$O_2CC_6H_5$	35
160 C-6-*endo*	CH_3	33
	C_5H_{11}-*n*	25
	C_4H_9-*t*	—
	C_6H_5	39
	$CH_2OCH_2C_6H_5$	23
	$CH_2O_2CC_6H_5$	40

$CH_2OSi(CH_3)_2C_4H_9$-*t*	26
$CH_2O_2CC_4H_9$-*t*	34

Steric effects on the regioselectivity of oxygen insertion of 6-*endo*-substituted-8-oxabicyclo[3.2.1]octan-3-ones **160** are shown in Table 6. (9, 38, 40) Conversions are below 50% with TFPAA after 36 hours at 25° in methylene chloride because of the low equilibrium concentrations of tetrahedral Criegee intermediates; a *tert*-butyl group blocks oxidation. The bulky substituent decreases the tendency for the nearest methylene carbon to migrate. This finding contrasts with the tendency in steroidal A-ring ketones for the more sterically hindered methylene to migrate preferentially, but can be explained. (267) In order for a group R_M in a tetrahedral Criegee intermediate to migrate to oxygen with ejection of carboxylic acid two prerequisites must be met. The groups R_M-C-O-O of **6** should have R_M and the distal oxygen in an antiperiplanar geometry. Additionally, one of the hydroxy nonbonding electron pairs must also be antiperiplanar to R_M. These requirements are met by conformation **7**, from which the C-2 carbon farthest from the group R can migrate. The conformation which results in migration of C-4 is disfavored by nonbonded repulsion of the group R and the hydroxy hydrogen, which must now be on the same side of the molecule as R. (9, 38, 40)



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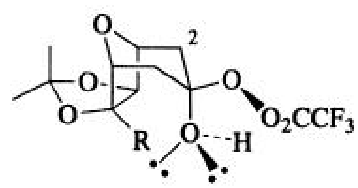

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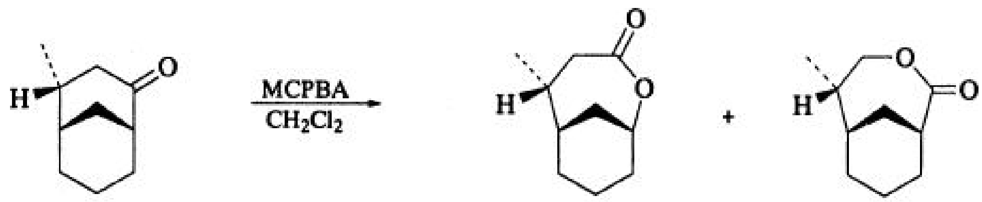
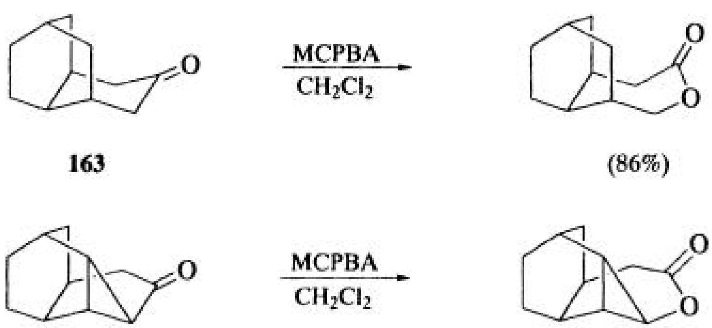
3.4.1.4. Oxidation of Bicyclo[3.3.1]nonanones

Bicyclo[3.3.1]nonan-2-one oxidizes with MCPBA (444) or TFPAA to give a bridgehead migrated lactone. (464) Oxidation of ketone **161** with peracetic acid gives mainly lactone **162**, an intermediate in the synthesis of *erythro*-juvabione. (465)



161 162 (81%) (14%)

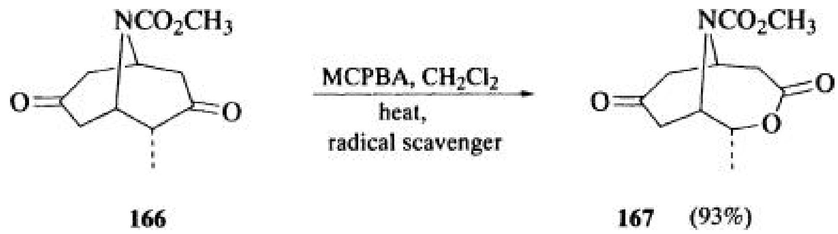
MCPBA does not oxidize bicyclo[3.3.1]nonan-3-one, (444) and the olefin of an internal C-6 double bond or a 7-*exo*-methylene on a bicyclo[3.3.1]nonan-3-one is more reactive than the C-3 carbonyl. (466-468)
Bicyclo[3.3.1]nonan-3,9-dione reacts only at the 9 position. (444) Failure of the 3-keto group in such systems to undergo Baeyer–Villiger oxidation is attributed to steric hindrance toward formation of the tetrahedral Criegee intermediate. In agreement with this reasoning, bicyclo[3.3.1]-nonan-3,7-dione (466, 469) and 7-*exo*-dicyanomethylenebicyclo[3.3.1]-nonan-3-one, (466) in which the olefin is deactivated toward electrophilic addition, are oxidized by MCPBA to lactones. Also, when the 7-*endo*-methylene hydrogen is tied back as in ketones **163** and **164**, MCPBA affords lactones. (444) Regioselective cyclopropyl migration to give **165** differs from the reactivity order of primary > cyclopropyl observed



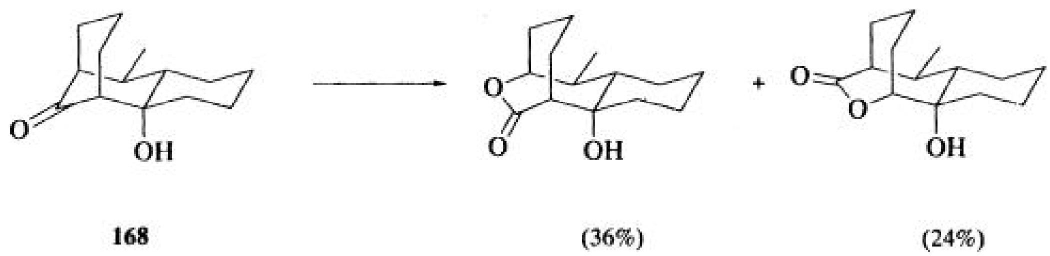
163 (86%)

164 165 (88%)

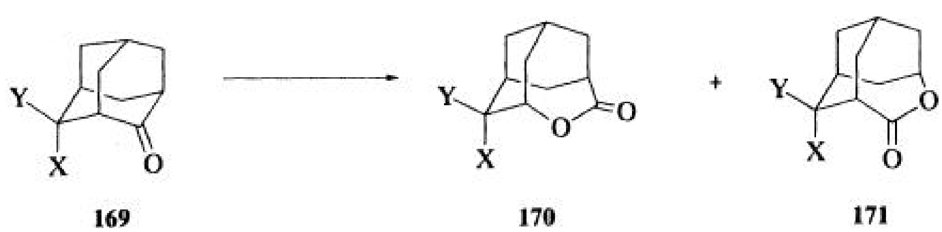
in oxidations of open-chain ketones. (42, 45) Chemoselective and regioselective oxidation of the 9-azabicyclo[3.3.1]nonan-3-one **166** provides the palustrine intermediate **167**. (470)



Bicyclo[3.3.1]nonan-9-ones oxidize with 40% peracetic acid, (471) monoperphthalic acid, (472) TFPAA, (473) or perseleninic acid. (474) A β -hydroxy group in **168** retards migration



of the α bridgehead. (475) Only migration of the distal bond to give lactones **171** is observed during PAA and MCPBA Baeyer–Villiger oxidations of *syn*-X and *anti*-Y 4-substituted adamantanones **169** with strongly electron-withdrawing methoxy, acetoxy, methanesulfonyl, and cyano substituents (Eq. 22). As shown by the percentages



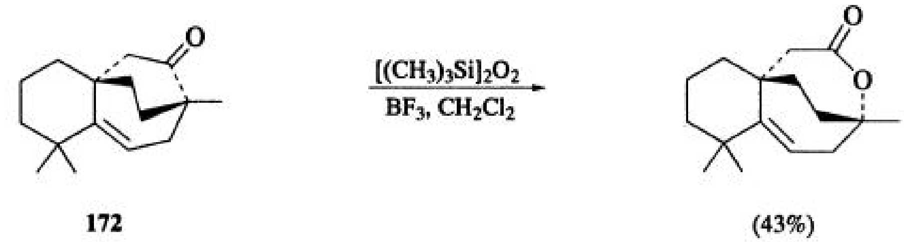
(22)

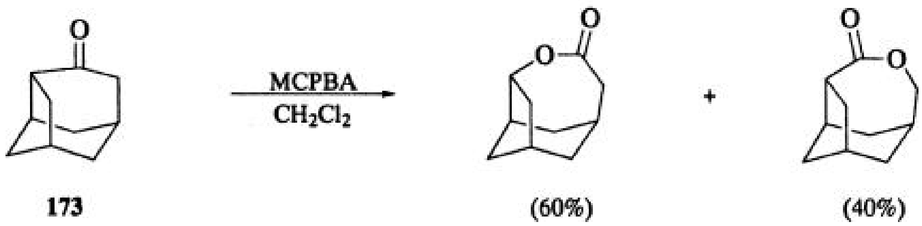
X or Y = OCH_3, O_2CCH_3, OSO_2CH_3, CN, Cl, Br, I, C_6H_5, H and H

in parentheses, less electron-withdrawing *anti*-Y/*syn*-X chloro (6%/7%), bromo (5%/20%), and phenyl (33%/50%) substituents afford increasing amounts of proximal bond migration product **170**. There is a moderate sensitivity to substituent stereochemistry. Iodo (71%/55%) adamantanones **169** give major lactone **170**, but hydrogen peroxide/selenium dioxide is used as the oxidant. The *syn* epimers are generally less reactive. (476)

3.4.1.5. Oxidation of Bicyclo[3.2.2]nonanones

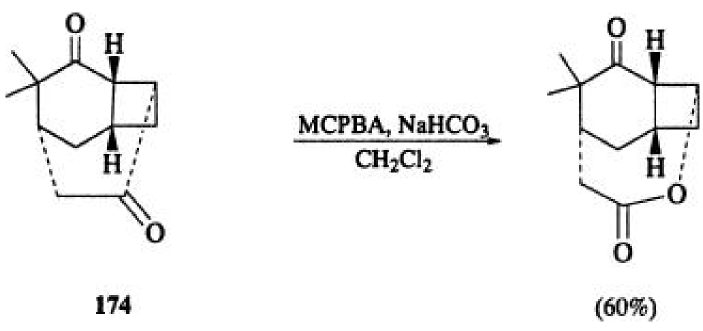
In a synthesis of widiol, the bicyclo[3.2.2]nonan-6-one derivative **172** is oxidized chemoselectively with *bis*-trimethylsilyl peroxide. (477) Bridgehead migration is preferred with MCPBA oxidation of 4-protoadamantanone **173**, a methylene-bridged bicyclo[3.2.2]nonan-6-one. (478)





3.4.1.6. Oxidation of Bicyclo[4.3.1]decanones

Bicyclo[4.3.1]decan-8-one retains sufficient conformational flexibility that Baeyer–Villiger oxidation succeeds after 240 hours with MCPBA. (444) Bicyclo[4.3.1]decane-8,10-dione reacts only at the C-10 carbonyl with MCPBA after 24 hours. (444) The tricyclic diketone **174** reacts regioselectively and chemoselectively with MCPBA solely at the less-hindered carbonyl. (479)

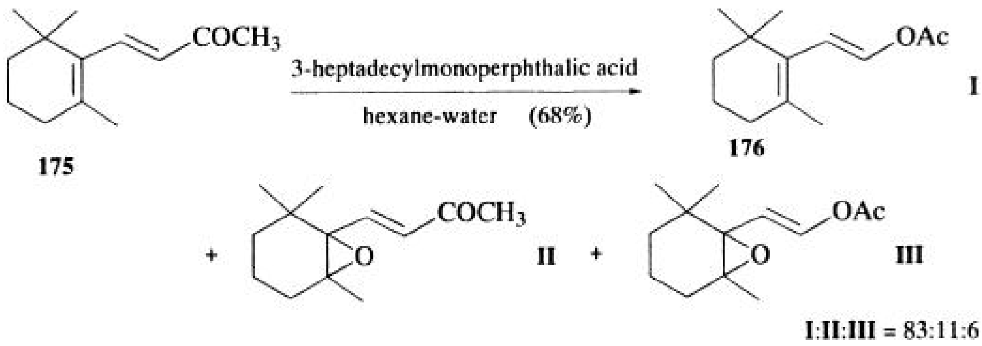


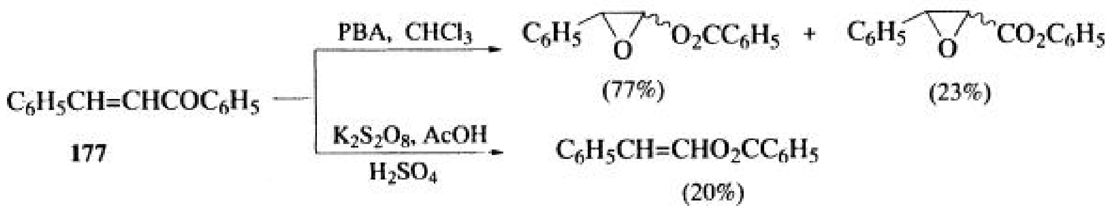
3.5. Reactions of α , β -Unsaturated Ketones

3.5.1.1. Oxidation of Acyclic Conjugated Ketones

Epoxidation of acyclic methyl vinyl ketones is often favored over Baeyer–Villiger oxidation.β -ionone **175** cannot be avoided using MCPBA or perbenzoic acid, (483, 484) the monosodium salt of

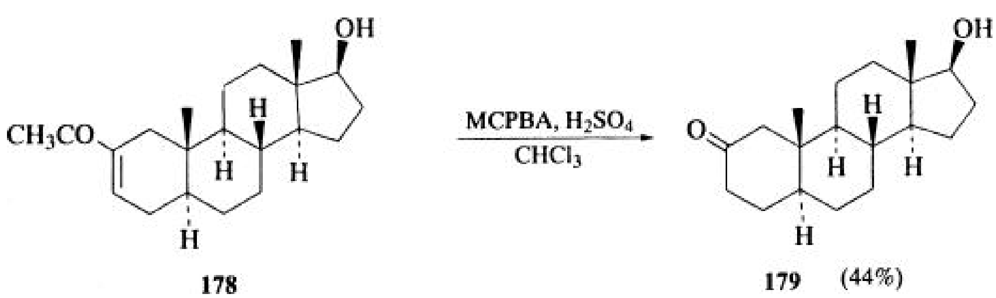
3-heptadecylmonoperphthalic acid in a hexane–water emulsion system gives mainly the enol ester **176**. (484) Oxidation of phenyl vinyl ketone **177** is only partially regioselective and is accompanied by olefin epoxidation; (485) however, persulfuric acid affords a small yield of enol ester. (486)





3.5.1.2. Oxidation of Monocyclic Conjugated Ketones

Monocyclic conjugated ketones are of three types depending upon whether the olefin and carbonyl groups are endocyclic or exocyclic to the ring. Cyclohexenyl methyl ketones, which have an endocyclic olefin and an exocyclic carbonyl, give primarily enol acetates and minor amounts of epoxy acetates with MCPBA. (487, 488) As part of a 1,2-ketone transposition method which begins with a 3-ketosteroid, cyclohexenyl ketone **178** is oxidized to

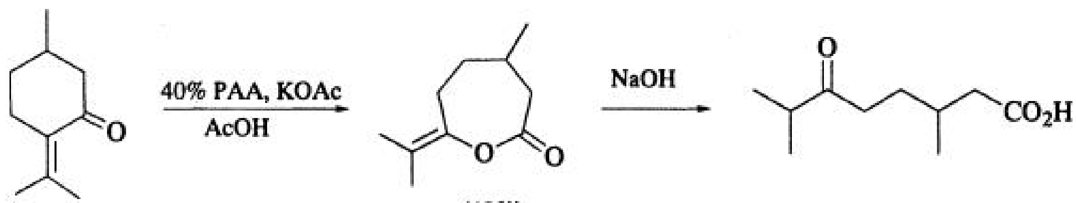


an intermediate enol acetate, which hydrolyzes to 2-ketosteroid **179**. (488) Cyclopentenyl ketone **180** affords only epoxyacetate with MCPBA; (488) however, the fused-ring ketone **181** yields an enol acetate. (489)

180 (35%)

181 (—)

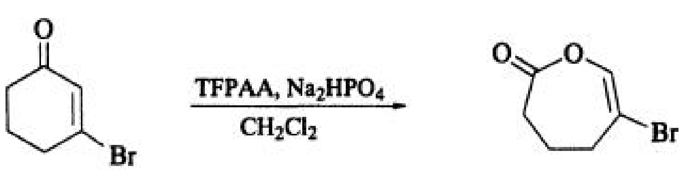
Peracetic acid or MCPBA convert *exo*-alkenylcycloalkanones mainly to enol lactones, (106, 490, 491) although minor amounts of epoxy ketone can be formed (Eq. 23). (106) Keto acids usually are isolated from reactions of *exo*-alkylidenecyclopentanones with basic hydrogen peroxide. (158, 179)



(40%)

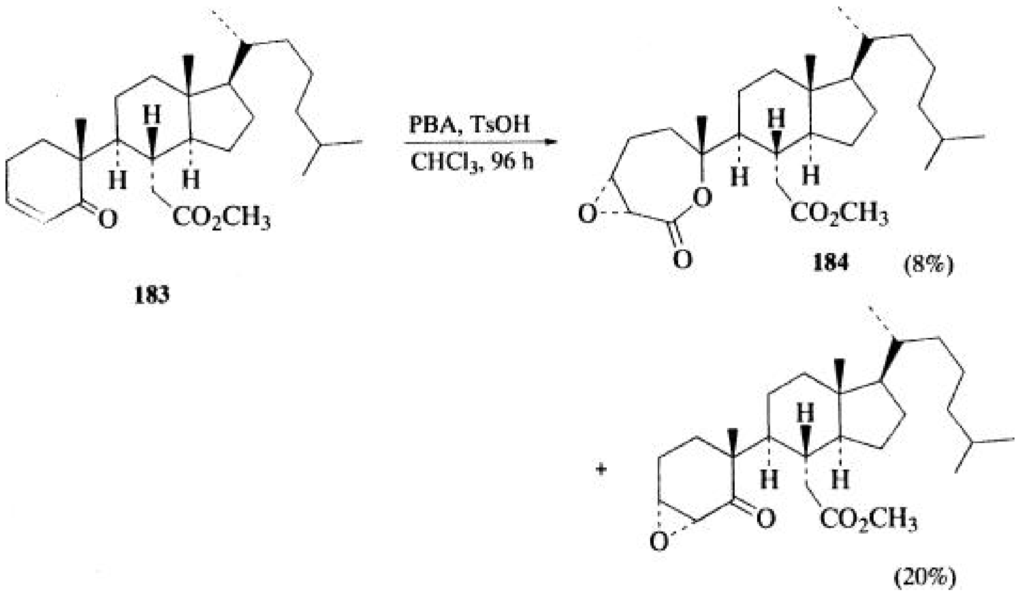
(23)

The regiochemical outcome of the Baeyer–Villiger oxidation of cycloalkenones, in which the olefin and carbonyl group are parts of rings, depends upon substitution adjacent to the carbonyl group. Vinyl migration generally is preferred over methylene migration to give ring-expanded enol lactones, (492, 493) as shown by the regioselective formation of lactone **182**. (493) Although epoxylactone **184** is formed from secocholestenone

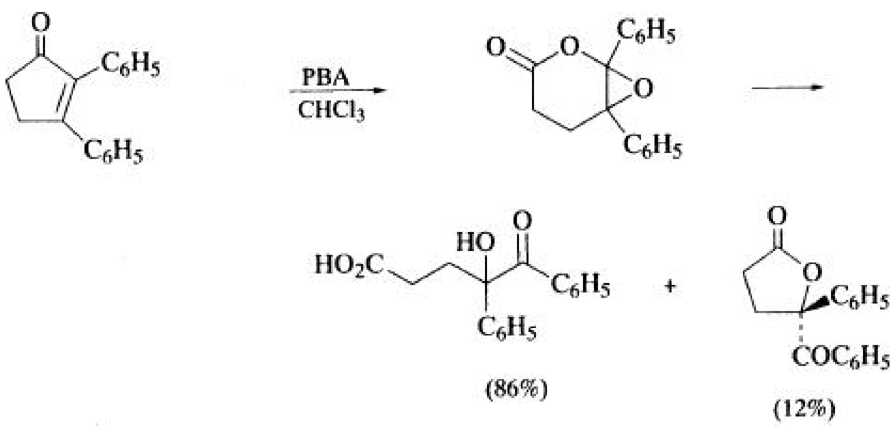


182 (68%)

183 by migration of the tertiary alkyl group, the yield is too low to infer a general principle for competitive migrations. (169)

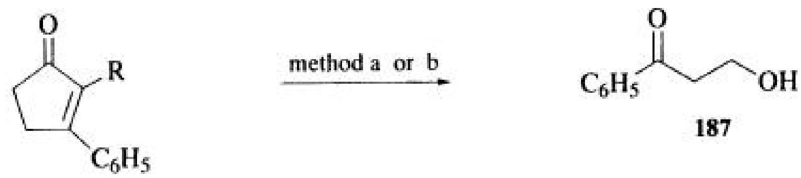


Potential problems during cycloalkenone oxidations include olefin epoxidation followed by rearrangements of the epoxylactone products (Eq. 24). (485) Further complications



(24)

may arise from base-catalyzed retrograde aldol condensations; keto acid **187** has been isolated following oxidation of cyclopentenones **185** and **186**. (485, 494)



187

185 R = H

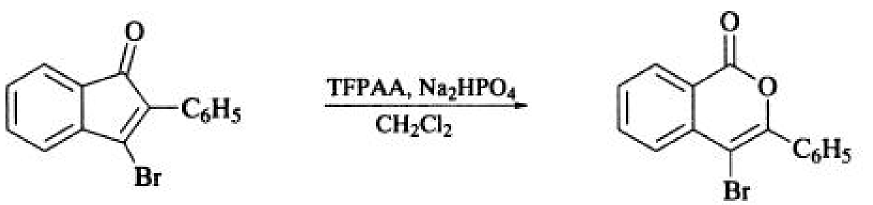
186 R = CH_3

method a. PBA, $CHCl_3$ (50%)

method b. 30% H_2O_2, NaOH, CH_3OH (58%)

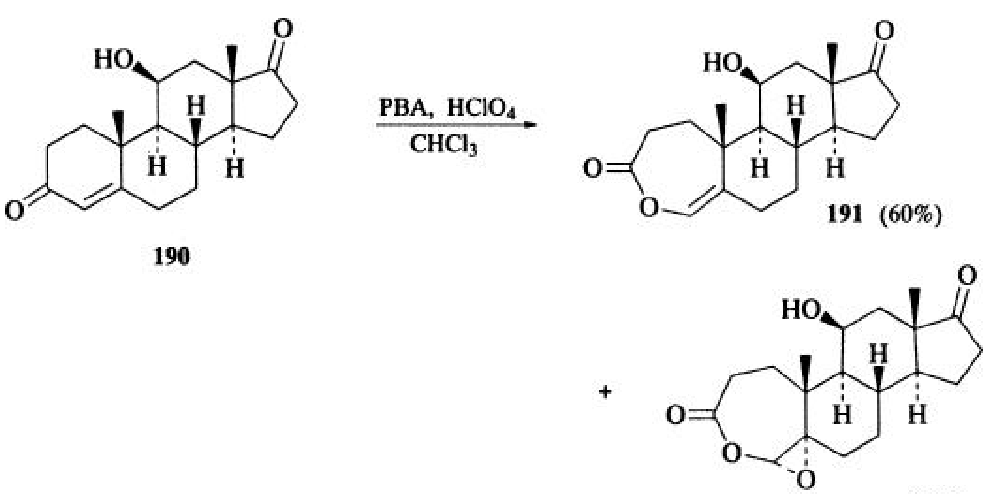
3.5.1.3. Oxidation of Fused-Ring Conjugated Ketones

Benz-fused cyclopentenone **188** affords lactone **189** by preferential vinyl migration. (493) Although the primary



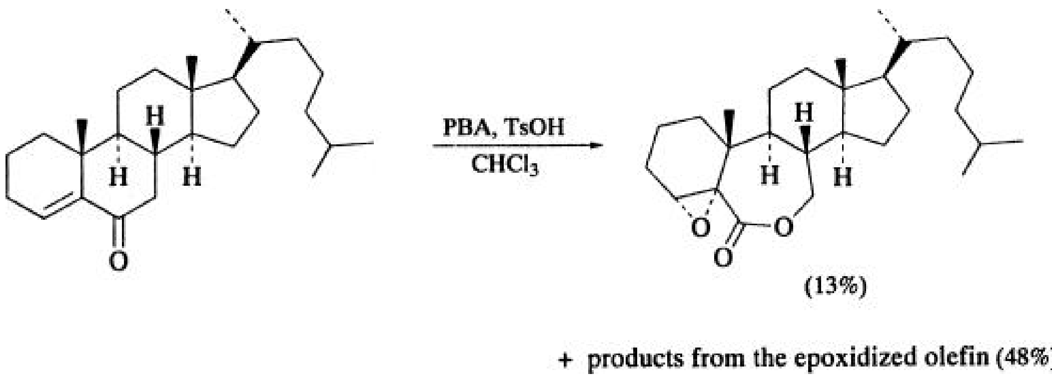
188 189 (82%)

Baeyer–Villiger oxidation product of a cycloalkenone flanked by a methylene group is usually an enol lactone formed by vinyl migration, (495) this product often is accompanied by a related epoxide. (281, 298, 305, 496, 497) An example is the chemoselective conversion of androst-4-en-3,17-dione **190** to enol lactone **191** and epoxylactone **192**. (281)



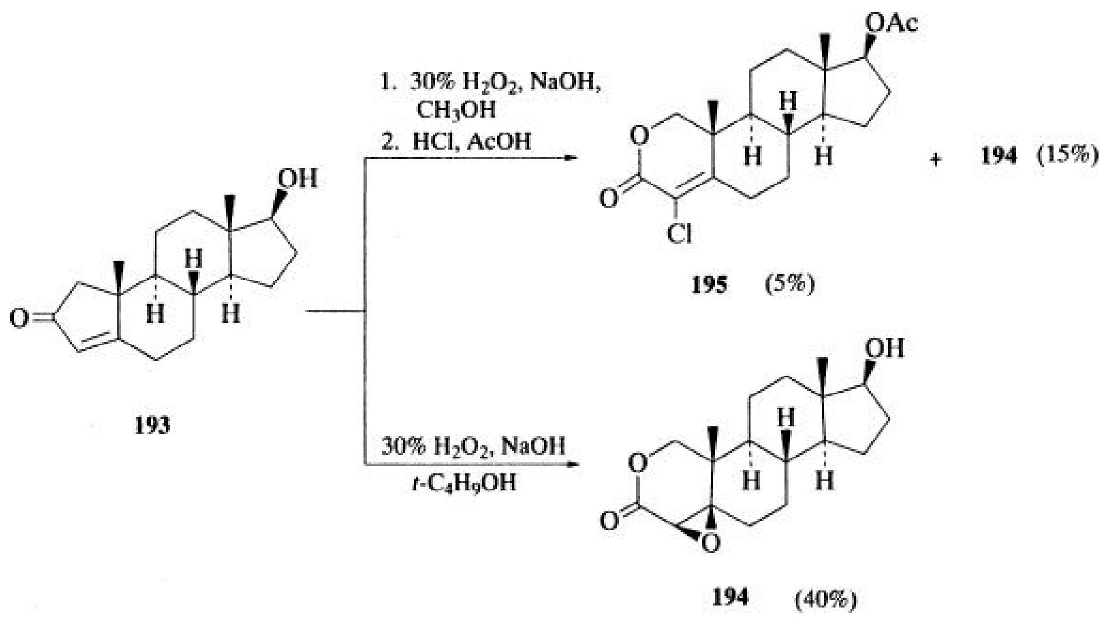
190 191 (60%) 192 (8%)

The general rule of preferential vinyl migration in the peracid oxidation of fusedring cycloalkenones has exceptions. Major migration of a methylene group in preference to vinyl is observed in the perbenzoic acid oxidation of cholest-4-en-6-one to give an epoxylactone as the only Baeyer–Villiger product (Eq. 25). (498) Oxidation of

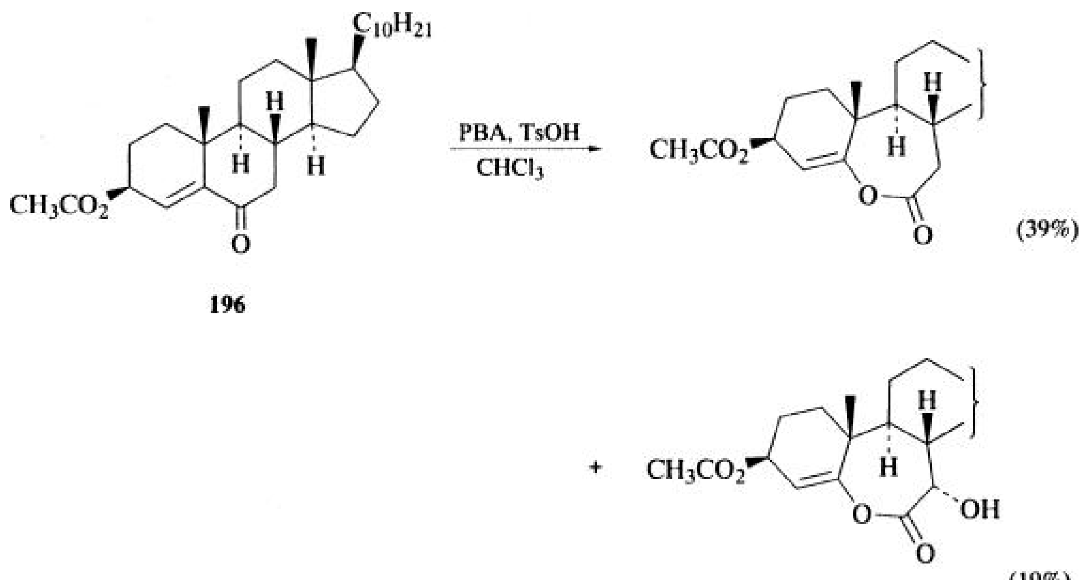


(25)

A-nortestosterone (**193**) with basic hydrogen peroxide affords epoxidized lactone **194** by way of methylene group migration; (299, 499) the epoxylactone **194** isomerizes upon acid workup to α -chloro conjugated lactone **195**.



Alternative reactivity modes are potential problems with conjugated ketones. With perbenzoic acid the 3- β -acetoxyketone **196** gives a mixture containing an α -hydroxy enol lactone **197**, which can arise from epoxidation of the enol form of

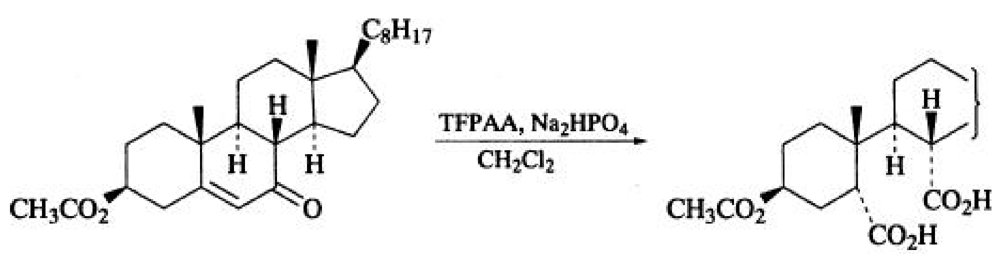


196

197

the ketone followed by subsequent rearrangement. (500) Hydroxylation of the saturated carbon adjacent to the carbonyl is observed with other steroidal-4-en-6-ones, (303, 501) and with the triterpene 11-keto- α -amyrone. (502) In other cases only products derived from olefin epoxidation may be formed, as when steroidal 3,5-diene-7-ones react with perbenzoic acid or performic acid. (503, 504)

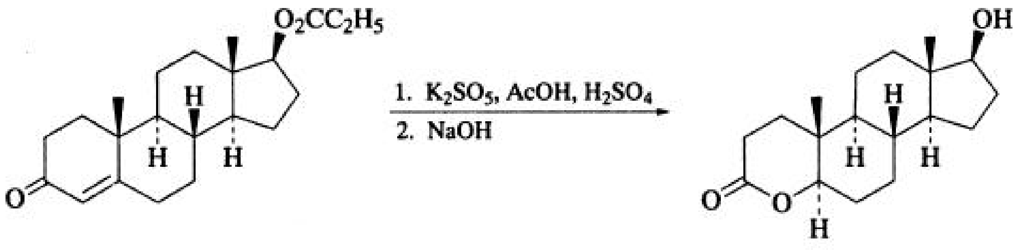
Further oxidation of aldehydes formed in situ can lead to numerous products. If an initially formed enol lactone undergoes ring opening, peracid can oxidize the revealed aldehyde to an acid. (505) Cholestenone **198** oxidizes to diacid **199** even in



198

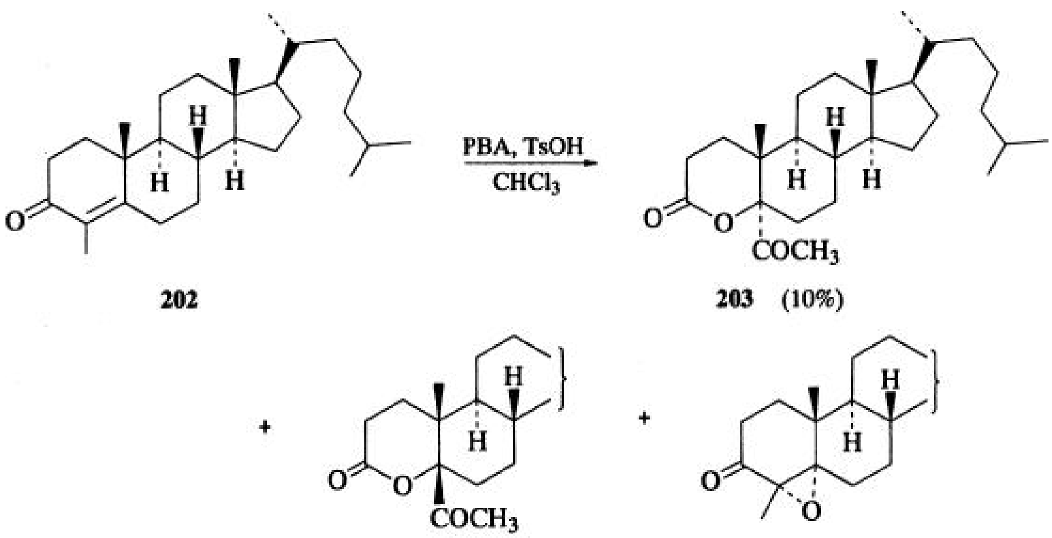
199 (—)

buffered TFPAA. (506) An aldehyde can also undergo further Baeyer–Villiger oxidation to a formate ester. (252, 507, 508) Oxidation of **200** gives lactone **201**, which can be formed



200 **201** (26%)

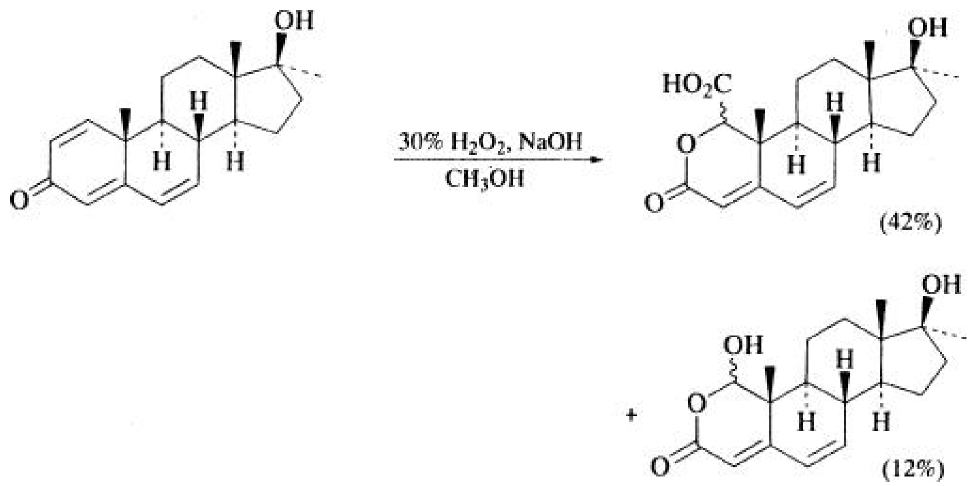
by the conversions: enol lactone →aldehyde acid→ formate ester acid → alcohol acid →lactone. (507)



202 **203** (10%) **204** (7%) (10%)

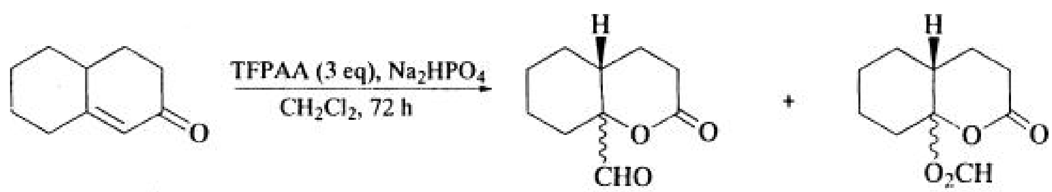
Ring opening of enol lactone epoxides in the presence of oxidant can result in a number of time- and peracid-dependent processes. The ring-opened α -hydroxy aldehyde or ketone can recyclize to a formyl- or acyl-substituted lactone. (298, 504, 508-513) An example is the ring opening and reclosure of the β -epoxy lactone formed during oxidation of cholestenone **202** to the mixture of acetyllactones **203** and **204**. (512)

Secondary oxidations of the α -hydroxyaldehydes, formed in situ from enol lactone epoxides, can occur. The aldehyde may oxidize to a carboxylic acid (Eq. 26). (514)



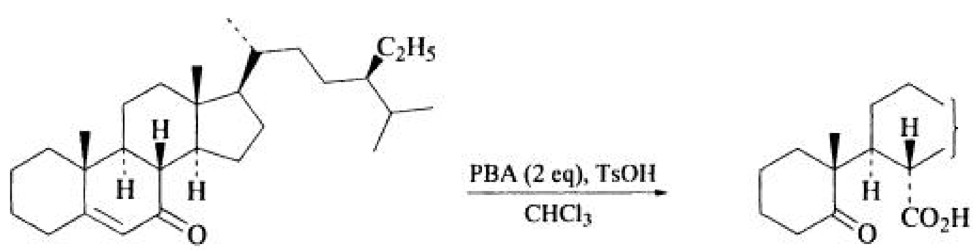
(26)

Alternatively, as is shown in the oxidation of the unsaturated decalenone **205**, (298) an intermediate formyl lactone **206** can oxidize further to formate ester **207**. (298, 508)



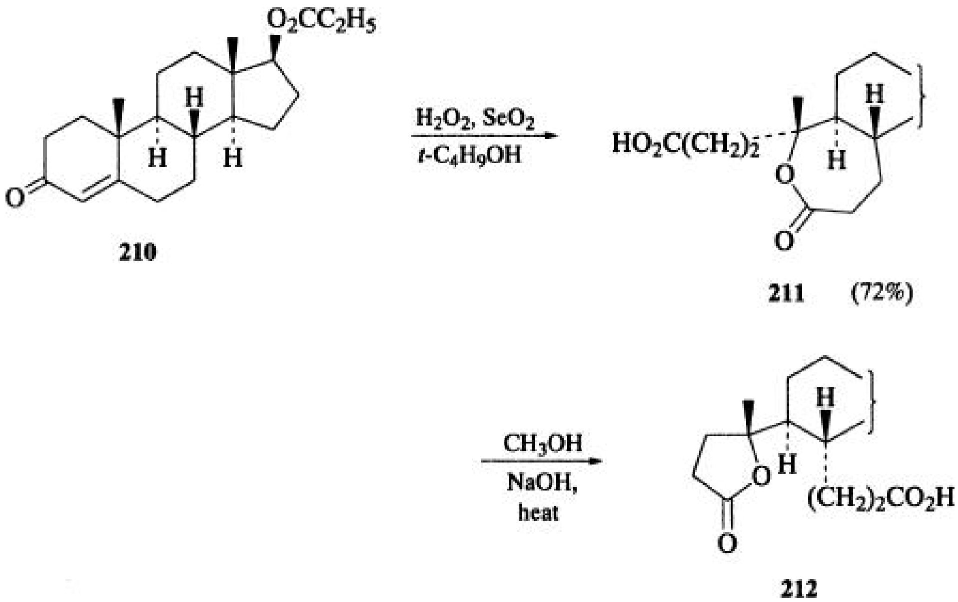
205 **206** (70%) **207** (30%)

If further hydrolysis occurs at the lactone formate ester oxidation level, the result is a ketoacid, which has lost one carbon as formic acid. (305, 501, 504, 509, 511, 513) An example of this process is the oxidation of the B ring of stigmastenone (**208**) to ketoacid

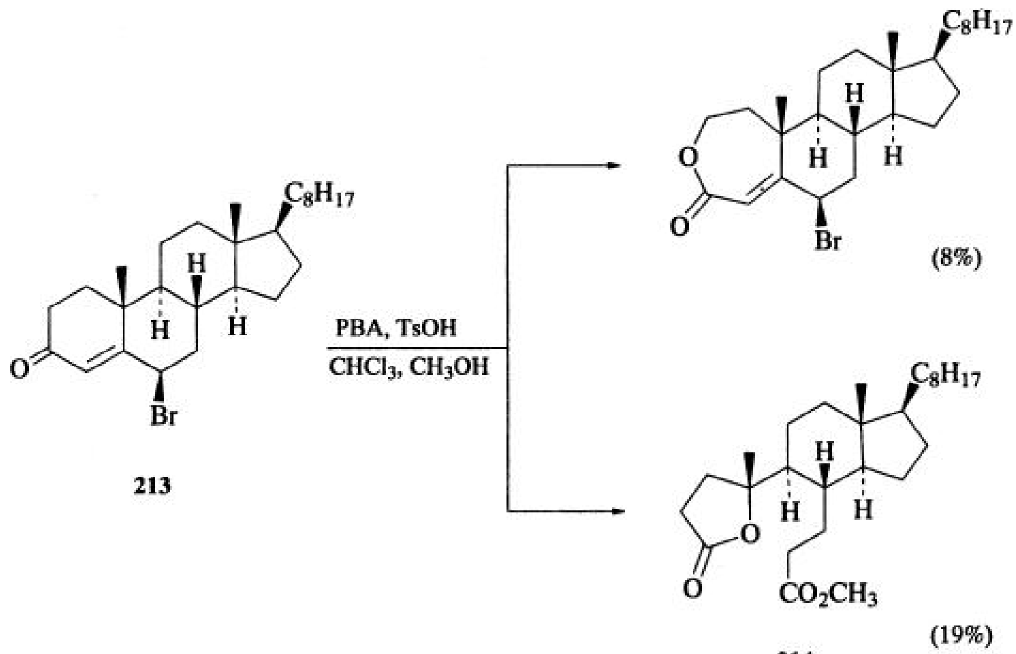


208 **209** (56%)

209. (504) The ketoacid formed in situ is subject to further Baeyer–Villiger reaction; the oxidation of testosterone propionate (**210**) shows conversion of the B ring to a lactone **211**, which is subject to ring opening and reclosure to lactone **212**. (101, 508, 515, 516)

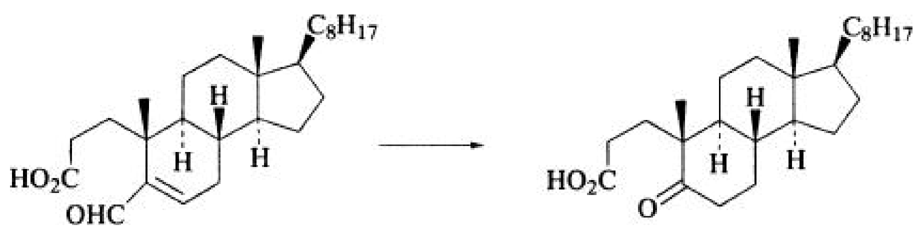


The presence of a γ halogen can lead to products resulting from an elimination reaction. In the oxidation of bromoenone **213**, formation of an enol lactone followed by hydrolysis and elimination of hydrogen bromide forms an intermediate aldehyde **215**. (516) A second Baeyer–Villiger oxidation and hydrolysis of the enol formate ester



213

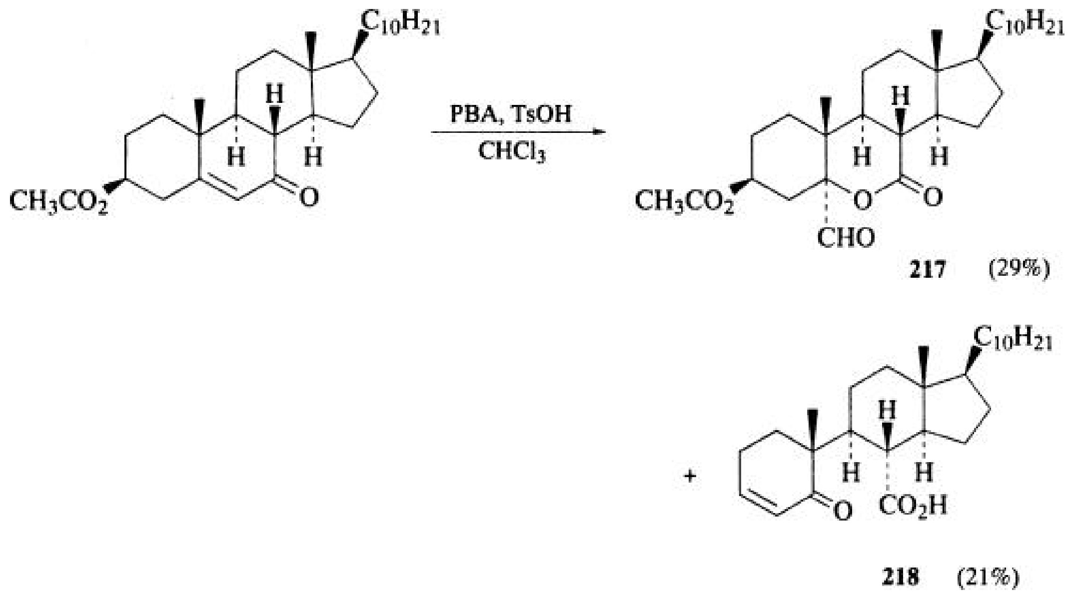
214



215

216

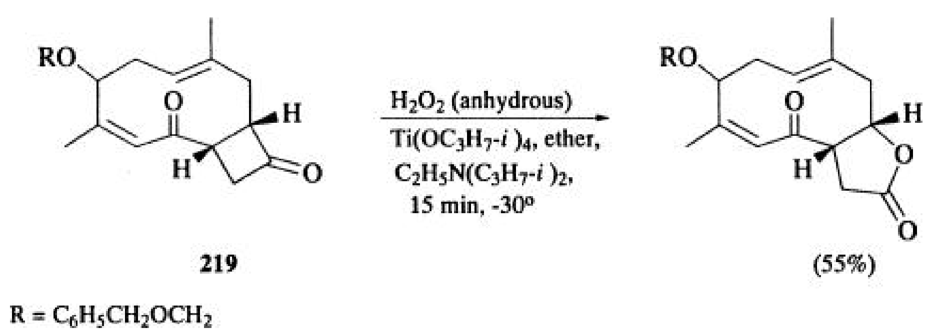
gives intermediate ketone **216**. A third Baeyer–Villiger oxidation with **216**, followed by ring opening and reclosure, provides lactone **214**. A homoallylic halogen or acetoxy group may also undergo elimination (Eq. 27). (504, 511, 513) Oxidation of the lactone



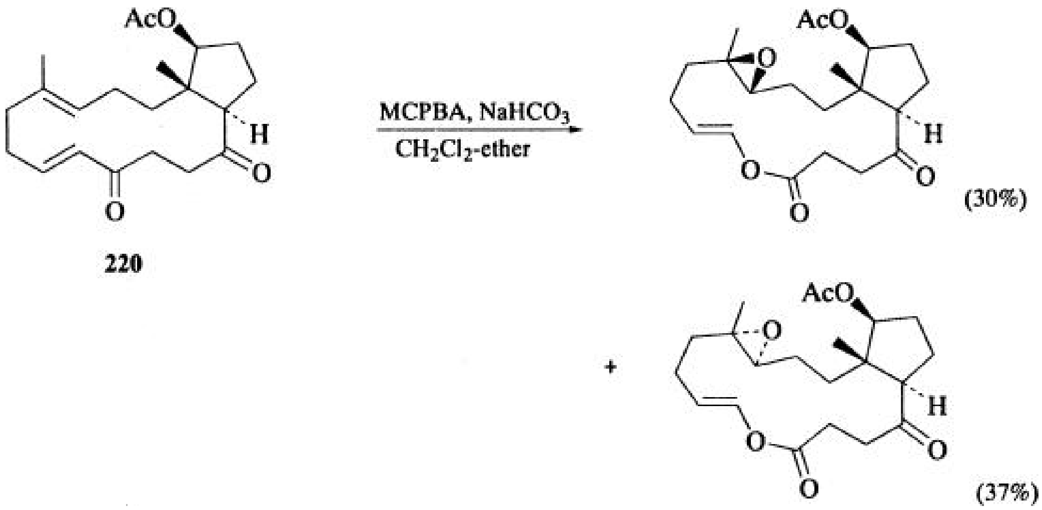
(27)

aldehyde **217** and hydrolysis of its derived hydroxyformate ester reveals a β -acetoxy ketone, which loses acetic acid to give enone **218**. (504)

The reactivity of cholest-5-en-7-one with MCPBA is reduced by a factor of 2–3 upon introduction of electron-withdrawing halogen or oxygen substituents at C-3- β . (517) A double bond also lowers reactivity, and 3-acetoxycholest-5-en-7-one is 15 times less reactive with MCPBA than 3-acetoxycholestan-7-one. (517) In molecules that contain conjugated and unconjugated ketones, the conjugated ketone often is either unreactive or is epoxidized. For example, in steroidal and triterpene ring systems perbenzoic acid effects Baeyer–Villiger oxidation at a C-3 carbonyl in preference to reaction with a 12-en-11-one functionality, (502) and a side-chain acetyl group can be converted to acetate with MCPBA in the presence of a hindered fused cyclohexenone. (108) Although 3 β -acetoxy-16-allopregnene-12,20-dione reacts selectively with perbenzoic acid to give Baeyer–Villiger oxidation of only the 12-ketone with migration of C-13, α -epoxidation of the C-16 double bond also occurs. (518) A reactive cyclobutanone **219** can be selectively oxidized with basic anhydrous hydrogen peroxide in the presence of an isolated olefin and a conjugated ketone. (236)



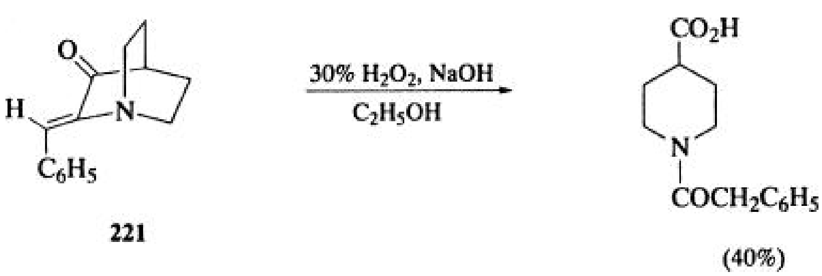
An example of selective Baeyer–Villiger oxidation of a conjugated ketone in the presence of a nonconjugated carbonyl is the MCPBA oxidation of diketone **220**. The reaction is accompanied by a nonstereospecific epoxidation of the isolated olefin. (519)



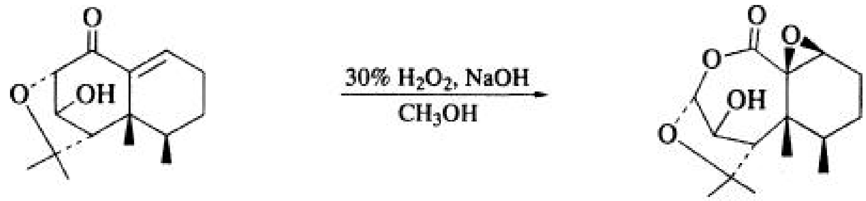
220

3.5.1.4. Oxidation of Bridged-Ring Conjugated Ketones

Basic hydrogen peroxide oxidizes the bridged bicyclic ketone **221**, which has an *exo*-alkylidene group, so that cleavage occurs between the carbonyl and vinyl group. (520) However, the bridged ketone **147** affords an epoxylactone **222** in which the oxygen-substituted bridgehead



221



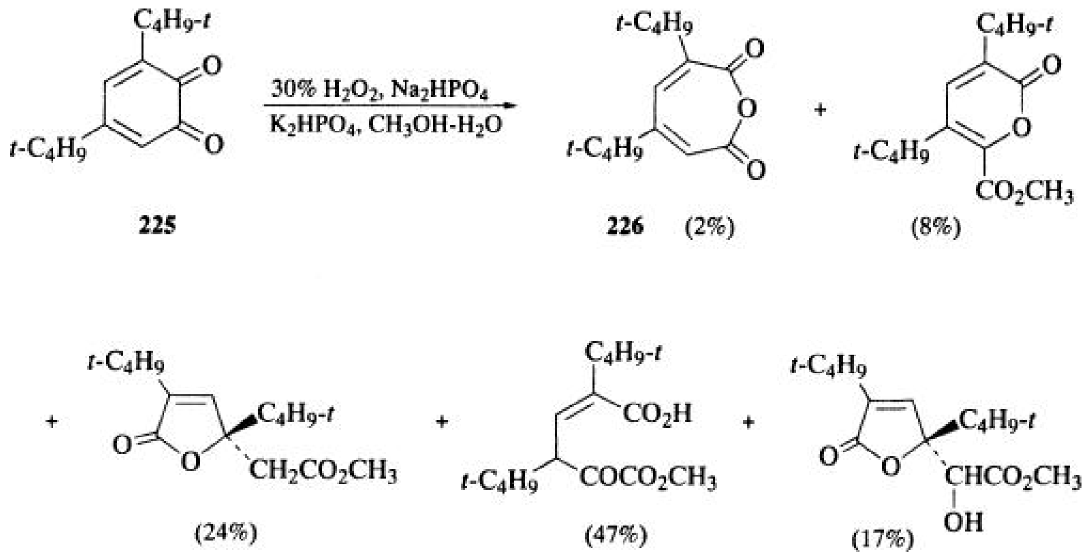
147 222 (43%)

has migrated. (433) Bridgehead migration without accompanying olefin epoxidation is reported in the MCPBA oxidation of tricycle **223** to the rearranged *exo*-methylenelactone **224**, whose putative structure is based upon ^{1}H NMR spectroscopy. (490)

223 224 (—)

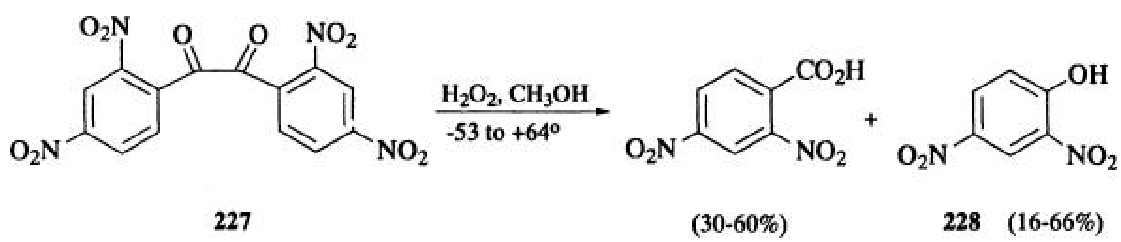
3.6. Reactions of 1,2-Dicarbonyl Compounds

Oxidation of α -diketones with MCPBA or monoperphthalic acid in inert solvents generally involves cleavage between the carbonyl groups to afford anhydrides, (218, 490, 521-527) while aqueous hydrogen peroxide (31, 528-536) or aqueous workup of peracetic acid oxidations provide carboxylic acids. (537) In alcoholic solvents acid esters can be formed. (538, 539) In the hydrogen peroxide oxidation of *o*-quinone **225** in methanol an initially formed anhydride **226** opens to an acid ester, which undergoes double bond oxidation and conjugate additions to give a mixture of products (Eq. 28). (31, 525)

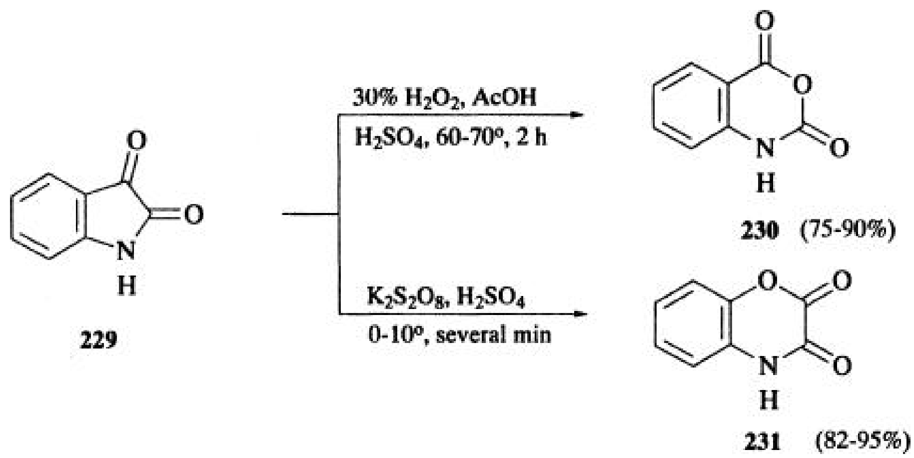


(28)

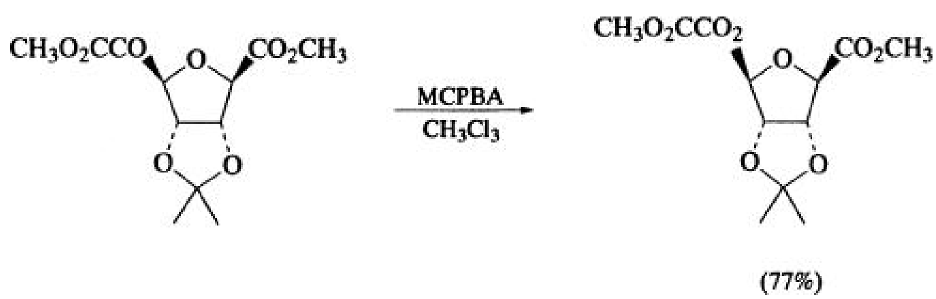
Oxidation of 2,2′4,4′-tetranitrobenzil (**227**) with methanolic hydrogen peroxide provides temperature-dependent mixtures of aryl and carbonyl migrated products. More 2,4-dinitrophenol (**228**) is formed at higher temperatures. (540)



The regiochemistry of oxidation of α -ketoamide **229**, and numerous aryl derivatives containing electron-donating ether and alkyl groups, as well as electron-withdrawing halogen and trifluoromethyl groups, is dependent upon oxidant. Insertion between the carbonyl groups to give anhydride **230** is observed with 30% hydrogen peroxide/acetic acid/sulfuric acid, while insertion adjacent to the ring to give lactone **231** occurs with persulfuric acid. (541)

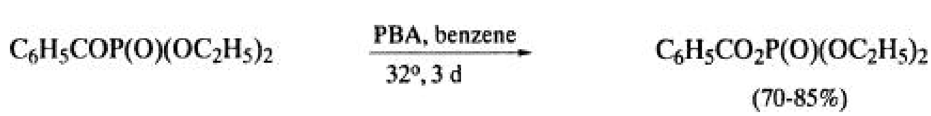


In a reaction which is part of the conversion of furan to L-ribofuranosides, tetrahydrofuranyl- α -ketoesters undergo regioselective migration of the carbon bearing the ring oxygen when oxidized with MCPBA (Eq. 29). (542, 543) Acylphosphites,



(29)

phosphorus analogs of α -keto esters, react with perbenzoic acid primarily to give acylphosphates (Eq. 30). (544)

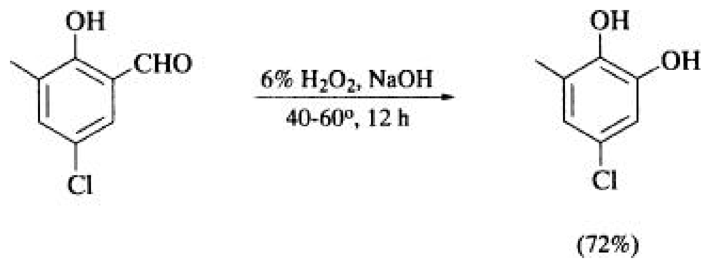


(30)

3.7. Reactions of Aldehydes

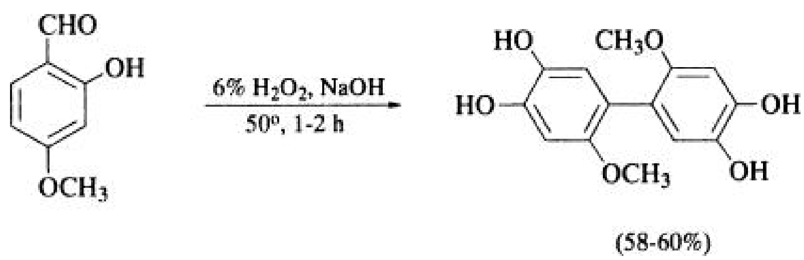
3.7.1.1. Oxidation of Aryl Aldehydes

Benzaldehydes containing hydroxy groups at the *ortho* or *para* position are converted to phenols by the Dakin oxidation using basic 3–6% hydrogen peroxide (Eq. 31). (96, 545-556) Polycyclic aromatic *o*-hydroxy- or



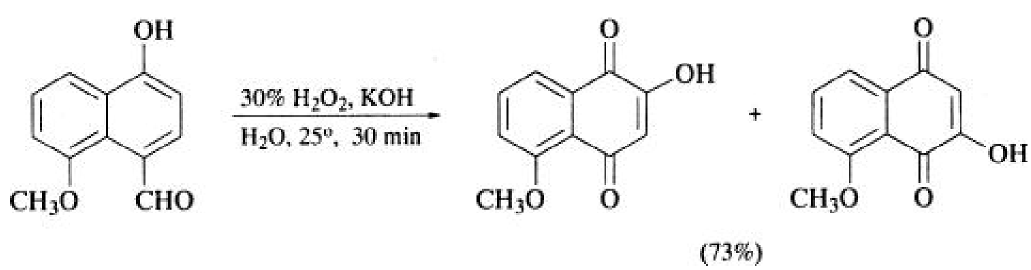
(31)

p-hydroxyaldehydes also undergo the oxidation. (557-566) An example of aryl coupling has been reported when heating was employed with a reactive substrate (Eq. 32). (550)



(32)

Stronger solutions of hydrogen peroxide (15–30%) are used occasionally, (567-570) however, oxidation to a quinone and ring hydroxylation may occur (Eq. 33) (571) Peracetic acid, (572, 573) which gives major amounts of quinones by overoxidation, potassium persulfate, (574)

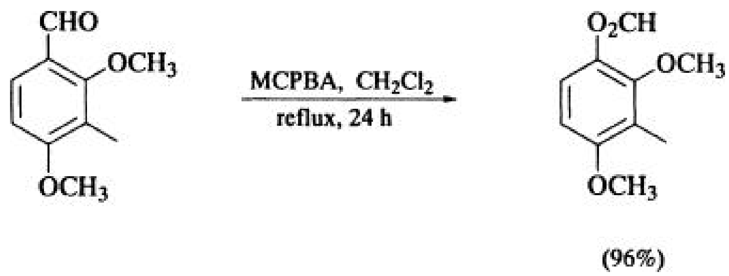


(33)

and MCPBA (575) are less effective oxidants for *o*-hydroxy- and *p*-hydroxybenzaldehydes.

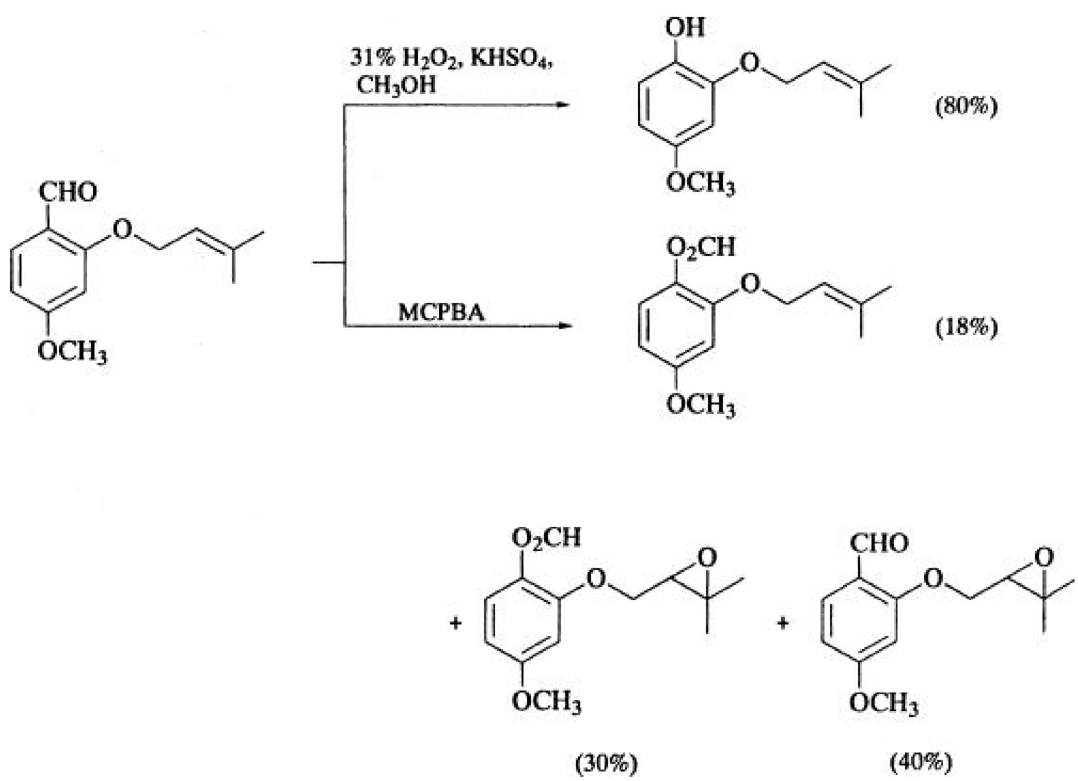
Benzaldehyde or benzaldehydes that have *ortho* or *para* alkoxy substituents are not effectively oxidized by basic hydrogen peroxide to give phenols. (546, 555) They can be oxidized to formate esters or the related phenols with 30% hydrogen peroxide catalyzed by areneseleninic acids, (576-578) acidic 31% hydrogen peroxide, (579) MCPBA, (575, 580-599) TFPAA, (589) dinitroperbenzoic acid, (600) performic acid, (591, 601-604) and peracetic acid. (572, 573, 605-609) A reaction used in the synthesis of mitomycin is shown in

Eq. 34. (584, 590, 591) Quinone formation, which can accompany oxidation of *p*-methoxybenzaldehydes with peracetic acid, (572, 573) is minimized by the use of lower reaction temperatures and shorter reaction times. (607)



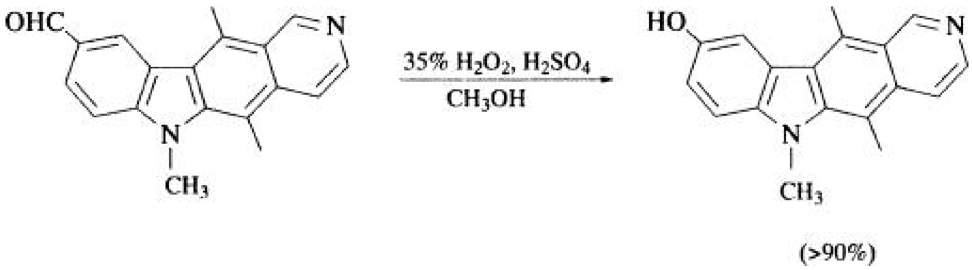
(34)

Oxidation of reactive aromatic aldehydes with *O*-allyl side chains is chemoselective for Baeyer–Villiger oxidation with acidic 31% hydrogen peroxide (579) or MCPBA. (610) Epoxidation of an isopropenyl side chain accompanies formate ester formation with MCPBA, but not acidic hydrogen peroxide (Eq. 35). (579) Chemoselective



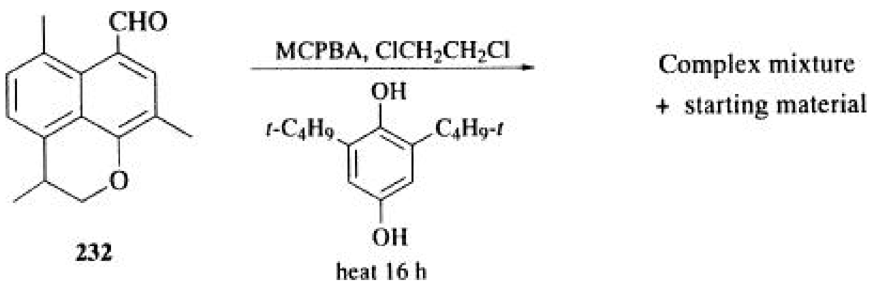
(35)

Baeyer–Villiger oxidations of reactive aromatic aldehydes are preferred over oxidation of pyridyl nitrogen in the presence of acidic 30–35% hydrogen peroxide (Eq. 36). (609, 611)



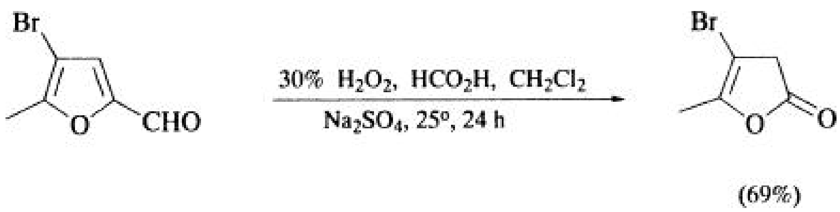
(36)

Steric hindrance toward attack of peracid on the formyl group precludes oxidation of naphthaldehyde **232**. TFPAA and MCPBA, even in refluxing 1,2-dichloroethane, fail to react. (612)



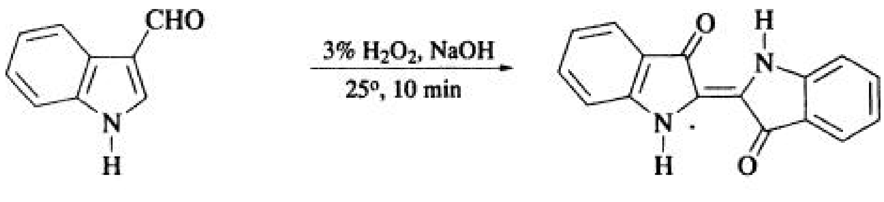
Aromatic aldehydes which have *m*-methoxy (578, 584) or *p*-methyl groups are best oxidized to phenols by 30% hydrogen peroxide containing *o*-nitrophenylseleninic acid (ONPSA). (578) Acidic 31% hydrogen peroxide gives mainly methyl esters with these substrates. (579) Phenols are obtained from benzaldehydes have a *p*-phenyl (577, 578) or fused aromatic rings using *o*-nitrophenylperseleninic acid, (578, 596) MCPBA, (571, 613, 614) or *p*-nitroperbenzoic acid. (615) Benzaldehyde is converted to benzoic acid by potassium persulfate. (574, 589) Similarly, there are no reported Baeyer–Villiger oxidations of benzaldehydes substituted only by electron-withdrawing chloro or nitro groups; acidic hydrogen peroxide converts such aldehydes to benzoate esters. (579)

Electron-rich heterocyclic aldehydes which undergo the Baeyer–Villiger oxidation include 2-formylfurans, (Eq. 37), (616, 617) *N*-(9)-methyl-3-formylcarbazole, (611) and *N*-(6)-methyl-9-formylellipticine. (611)



(37)

A coupling product **234** is formed upon oxidation of 3-formylindole (**233**). (546) Electron-poor 3-formylisoquinoline is oxidized to the carboxylic acid by 30% hydrogen peroxide. (618)

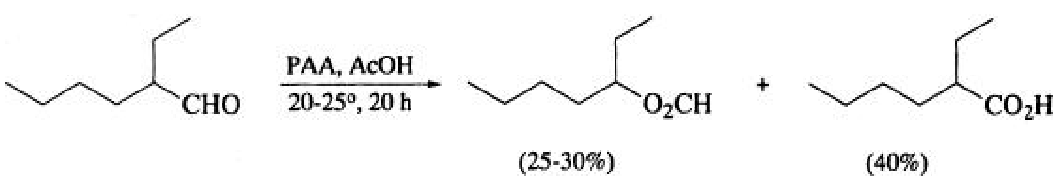


233

234 (70%)

3.7.1.2. Oxidation of Alkyl Aldehydes

Primary aliphatic aldehydes are oxidized mainly to carboxylic acids by peracetic acid or MCPBA. (589, 619) However, if the α -carbon is benzylic or secondary, formate ester formation generally is competitive with carboxylic acid formation using MCPBA, (620-622) peracetic acid, (589, 623) or TFPAA as oxidants (589, 619) (Eq. 38). An α oxygen facilitates formate ester formation (Eq. 39). (298)



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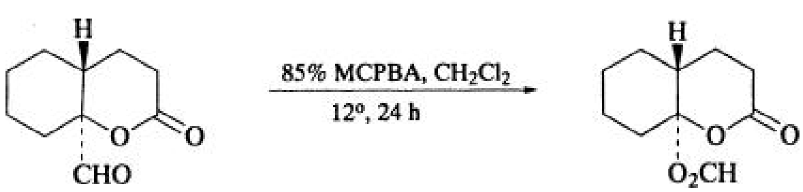
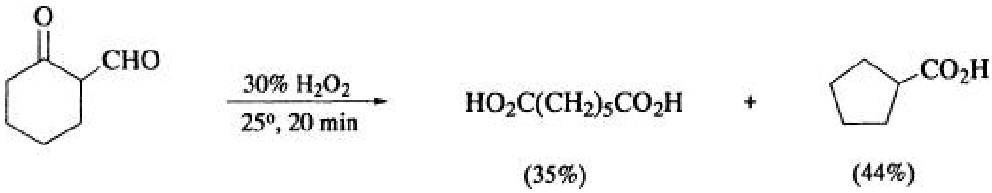


(39)

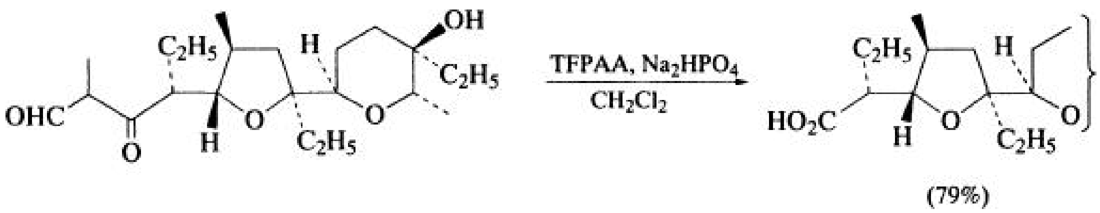
3.7.1.3. Oxidation of β -Ketoaldehydes

The oxidation of 2-formylcyclohexanones and 2-formylcycloheptanones by hydrogen peroxide affords a mixture of diacid and ring-contracted acid products (Eq. 40). (78, 81, 82, 202-204, 624) Shorter-chain diacids can be



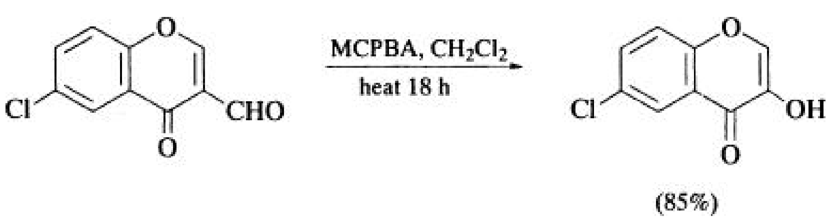
(40)

observed. (202, 204, 625) Straight-chain β-ketoaldehydes and 2-formylcyclopentanones give only cleavage products. (202, 203, 624) A method for directed chain cleavage of an ethyl ketone toward the primary substituent involves formylation of its kinetic enolate and oxidative cleavage of the derived ketoaldehyde (Eq. 41). (80)



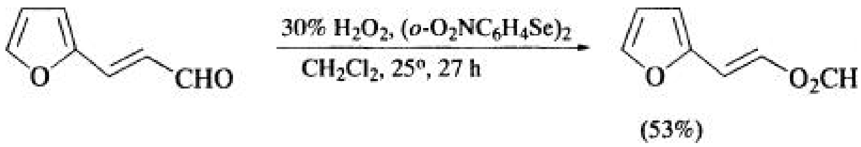
(41)

3.8. Reactions of α , β -Unsaturβ -unsaturated aldehydes to vinyl formates occurs with peracetic acid, (623, 626) *p*-nitroperbenzoic acid, (627) and MCPBA. (600, 628, 629) An example is shown in Eq. 42. (629) A study of oxidations with 30 and 90% hydrogen peroxide



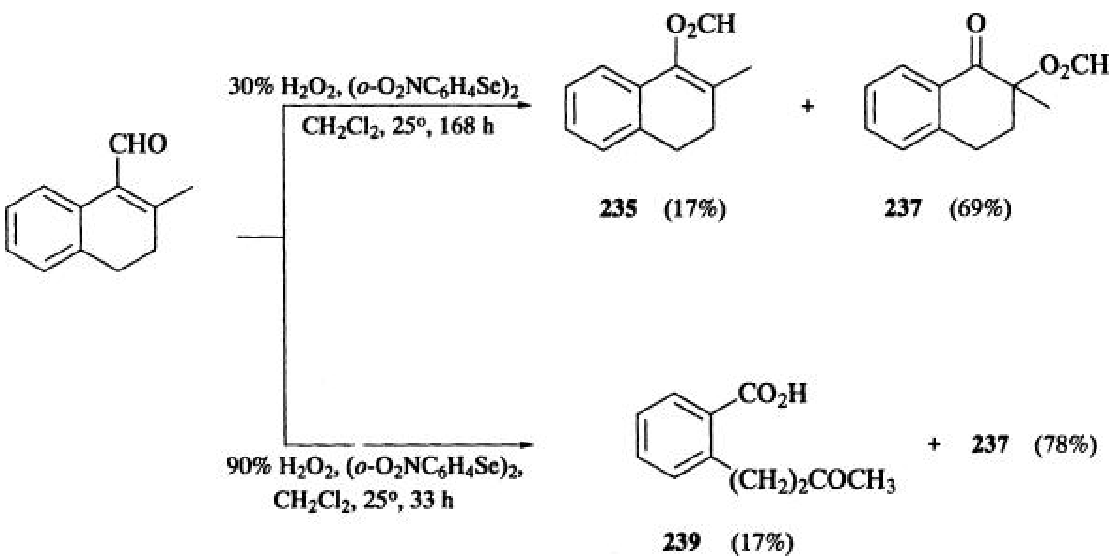
(42)

catalyzed by benzeneseleninic acids found that *bis*-*o*-nitrophenyl diselenide is the most effective catalyst for vinyl formate formation; the furan ring and double bond are not oxidized under these conditions (Eq. 43). (628) This catalyst–oxidant combination appears to be the favored method for vinyl formate formation when comparisons with MCPBA have been made. (628)



(43)

Overoxidation may accompany Baeyer–Villiger oxidation (Eq. 44). (600, 623, 627) Epoxidation of vinyl formate **235** gives epoxyformate **236**, which rearranges to ketoformate **237**. Further oxidation gives formyloxylactone **238**, which hydrolyzes to ketoacid **239**. (600) Overoxidation is most usual after long reaction times and if peracids or 90% hydrogen peroxide catalyzed by arylseleninic acids are used as oxidants. Basic hydrogen peroxide converts unsaturated aldehydes mainly to epoxy formate esters, (627) unless the olefinic bond is especially unreactive as in formylazulene. (630, 631)



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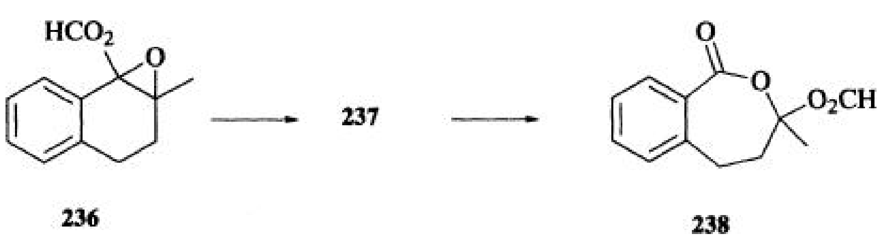


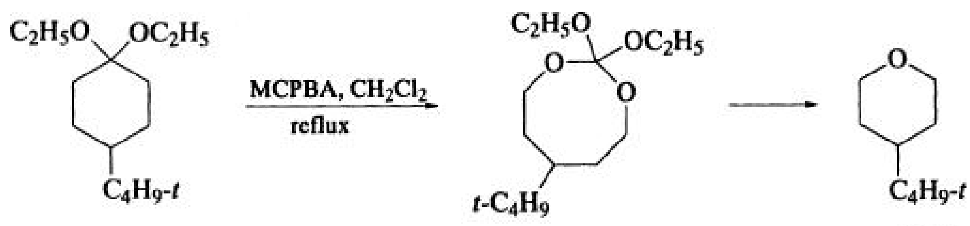
3.9. Peracid Reactions with Ketals and Acetals

Open-chain diethylketals can undergo a formal double Baeyer–Villiger oxidation to carbonate orthoesters upon treatment with MCPBA. (632, 633)

This oxidation results in a chain cleavage at both sides of the carbonyl carbon (Eq. 45). (632) Diethylketals of

$$n\text{-}C_7H_{15}C(OC_2H_5)_2C_7H_{15}\text{-}n \xrightarrow[\text{3. LiAlH}_4]{\text{1. MCPBA, CH}_2\text{Cl}_2;\ \text{2. HCl}} \underset{(75\%)}{n\text{-}C_7H_{15}OH} \qquad (45)$$

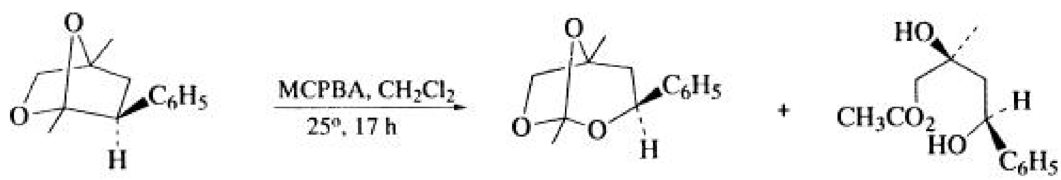
cyclopentanones and cyclohexanones, but not cycloheptanones, are also converted by MCPBA to carbonate orthoesters; (632, 633) these can rearrange to cyclic ethers if the reaction is carried out at reflux (Eq. 46). (632) Although cyclic ketals of ethylene glycol



(40%)

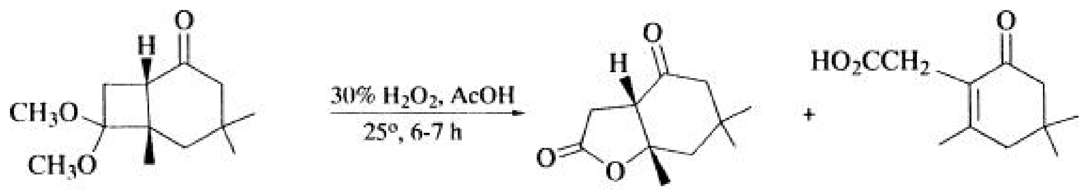
(46)

are stable to this oxidation, bridged oxabicyclo[2.2.1]heptane ketal **240** is oxidized to the ortho ester level. (634, 635)



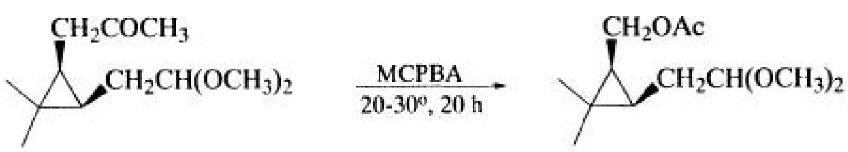
240 (53%) (26%)

Cyclobutanone dimethylketal **241** is oxidized chemoselectively to the butyrolactone **242** by aqueous peracetic acid. (111) Dimethylketals of cyclohexanone (232) and cyclopentanone (636) survive MCPBA during the oxidation of oxidizable carbonyl groups.



241 **242** (81% of a mixture)

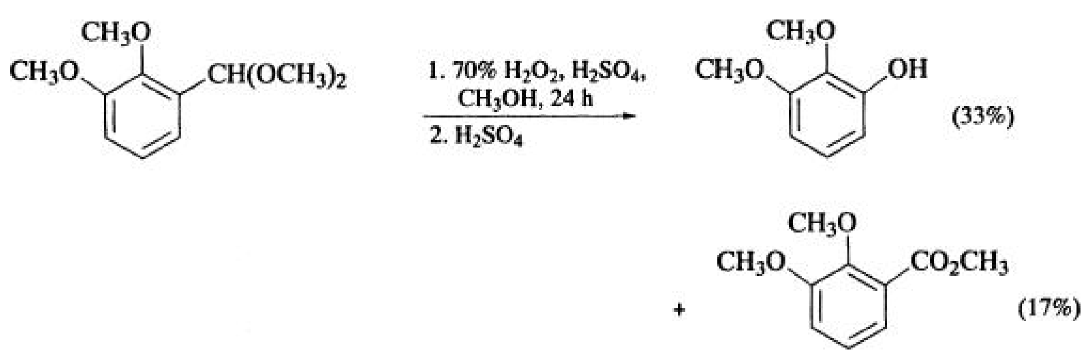
Although the acetal function of **243** is less reactive than the methyl ketone side chain, (637, 638) in the absence of a competing functionality a variety of acetals can be oxidized by peracids (Eq. 47) (639). Aryl migration has been observed (Eq. 48) (579), but usually esters are formed by loss of the hydrogen atom of the aldehyde. (639) A one-step conversion of γ -lactol methylacetals to γ -butyrolactones utilizes MCPBA in boron trifluoride etherate. (640) The one-step oxidation of diacetal **244** to dilactone **245** is superior to a two-step hydrolysis and oxidation. (641) The oxidation is not useful for δ -lactols. (640)



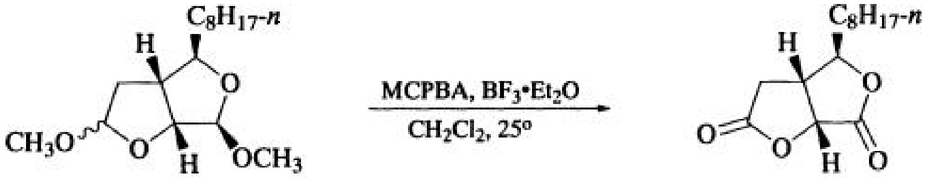
243 (75%) (47)

$$CH_3CH{=}CHCH(OC_4H_9\text{-}n)_2 \xrightarrow[60^\circ,\ 1\ h]{23\%\ PAA,\ AcOC_2H_5} CH_3CH{=}CHCO_2C_4H_9\text{-}n$$

(70%)



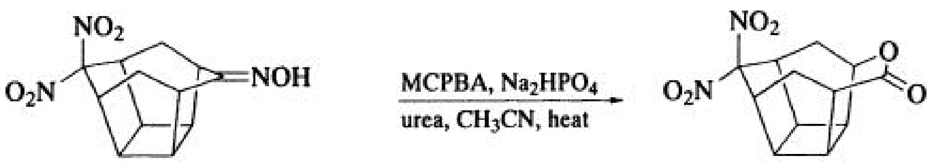
(48)



244 245 (80%)

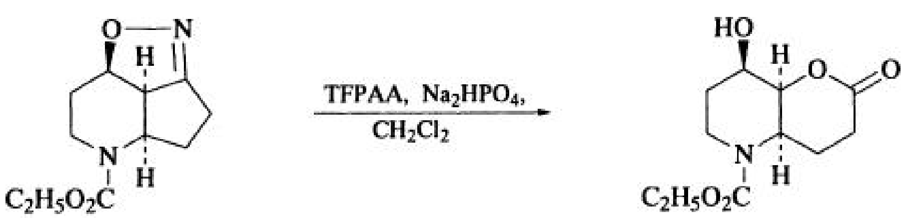
3.10. Peracid Reactions with Nitrogen Derivatives of Ketones and Aldehydes

The Baeyer-Villiger oxidation can be carried out on nitrogen-containing ketone derivatives. Oximes of caged ketones are oxidized to lactones with 90% hydrogen peroxide/fuming nitric acid (439) or MCPBA (Eq. 49), (642) and peracetic acid or MCPBA



(52%) (49)

affords a lactone from the oxime of 5- α -3-cholestanone. (240, 643) Isoxazolines are oxidized by excess TFPAA or 3,5-dinitroperbenzoic acid to lactones of β -hydroxyketones (Eq. 50). (85) Yields are comparable to those of a two-staged hydrogenolytic cleavage of the isoxazoline followed by Baeyer–Villiger oxidation.



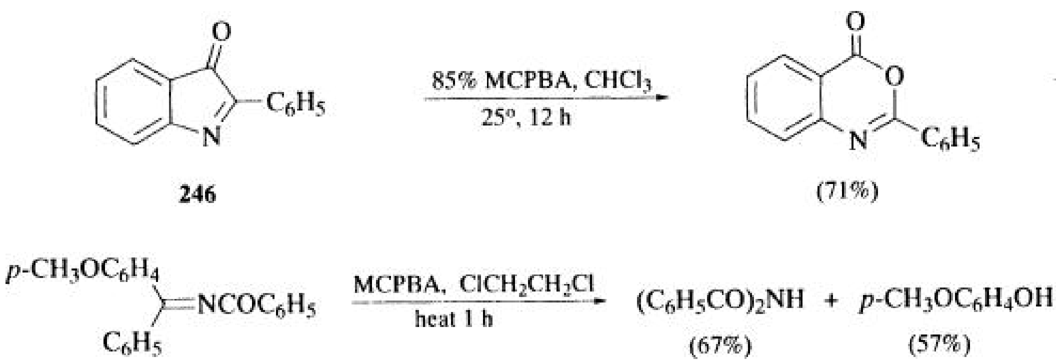
(42%) (50)

TFPAA effects cleavage of α -ketooximes primarily to diacids, although some oxidation of the oxime to a nitro group occurs (Eq. 51). (201) Oxygen is also inserted

$$C_6H_5COC(=NOH)CH_3 \xrightarrow[CH_2Cl_2,\ 1\ h]{TFPAA,\ Na_2HPO_4} \underset{(41\%)}{C_6H_5CO_2H} + \underset{(29\%)}{C_6H_5CO_2CH(NO_2)CH_3} + \underset{(5\%)}{C_6H_5O_2CCH(NO_2)CH_3} \quad (51)$$

between the ketone and imine double bonds upon treatment of 3-oxoindolenine **246** with 35% hydrogen peroxide (644) or MCPBA. (645)

N-Benzoyldiarylimes are oxidized to a mixture of phenol and imides (Eq. 52). (646) An attempt to prepare an epoxide of an *N*-acylenamine **247** led to oxidative ring



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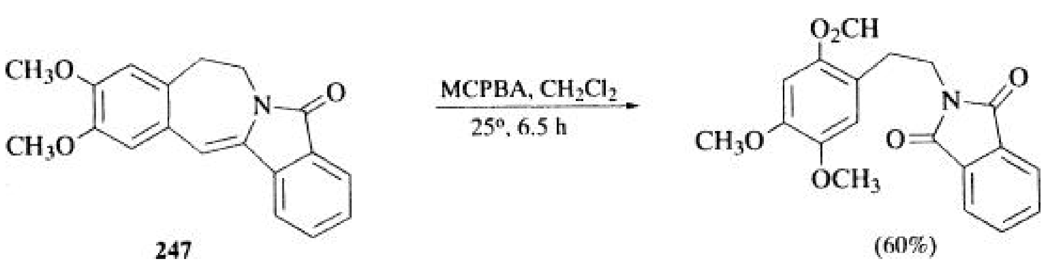
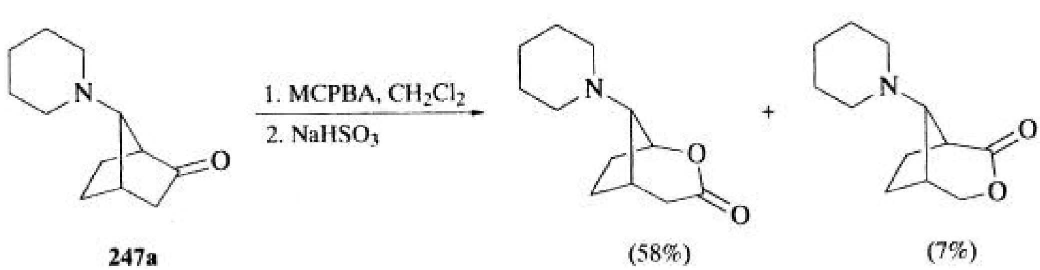
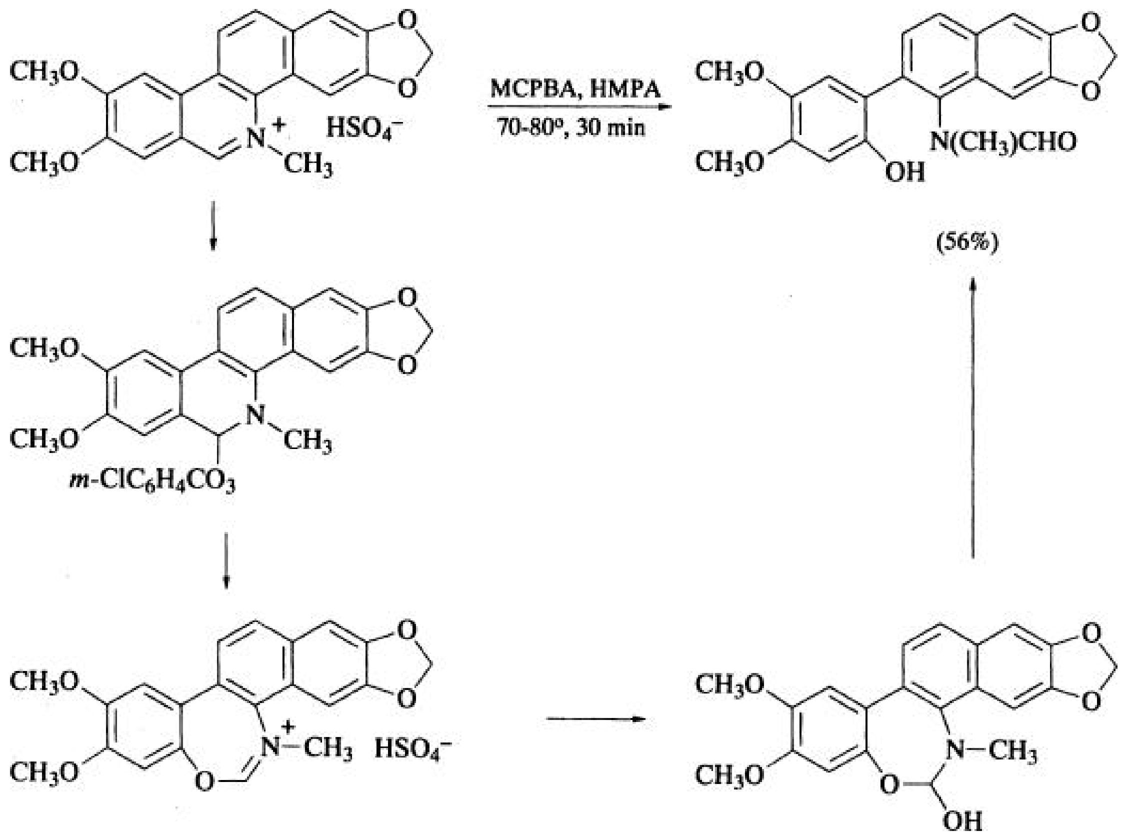




opening and Baeyer–Villiger oxidation of the released arylaldehyde. (597) *N*-Alkyliminium ions of amines and aryl aldehydes also react with MCPBA to form arylformate esters, most probably as shown in Eq. 53. (647, 648) The weaker oxidant *N*-benzoylperoxycarbamic acid does not form Baeyer–Villiger products with azines or imines. (649)



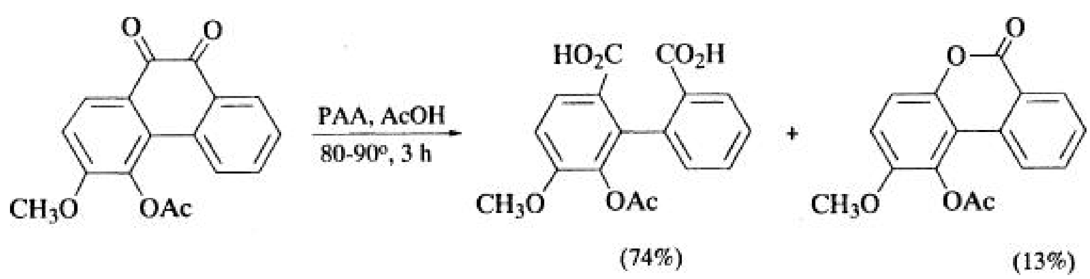
(53)

3.11. Competitive Side Reactions

Reactions of substrates to give products other than those of the normal Baeyer–Villiger oxidation are considered to be side reactions for purposes of this section. Side reactions can occur because of the oxidizing nature of the Baeyer–Villiger reagent, the acidic or basic nature of the reaction medium, or the reaction workup conditions. In prior sections of this review, where applicable, oxidations of double bonds, nitrogen, sulfur, and selenium atoms have been discussed. (2) Baeyer–Villiger oxidation of amine-containing substrates have been reported with and without *N*-oxide formation; for example, the piperidinyl group of *anti*-7-(1-piperidinyl)bicyclo[2.2.1]heptan-2-one (**247a**) is almost immediately oxidized by MCPBA to its *N*-oxide, whereas a reductive workup using sodium hydrogen sulfite is necessary to obtain the mixture of aminolactones. (371c) Separate sections of this review have been devoted to oxidations of carbon–nitrogen double bonds and to ketals and ketones formed by loss of the ketal protective group. Rearrangements and subsequent oxidations during

Baeyer–Villiger oxidation of α , β -unsaturated ketones have been discussed in the section devoted to those ketones. Other oxidative and rearrangement processes occasionally observed are discussed here.

There are less common oxidative processes that can accompany or defeat the desired Baeyer–Villiger oxidation. Ketone enolates can undergo olefin epoxidation to provide α -hydroxyketones. (70, 303, 501, 502) MCPBA is capable of oxidizing secondary alcohols to ketones. (2, 650) Persulfate ion hydroxylates formyl or acyl substituted phenols and arylamines. (651) Benzaldehyde and aromatic ketones can be hydroxylated by hydrogen peroxide catalyzed by antimony pentafluoride–hydrogen fluoride without Baeyer–Villiger oxidation. (652) Occasionally electrophilic attack by MCPBA or peracetic acid occurs at an *ipso* position with resulting loss of the *ipso* substituent (Eq. 54). (320, 537) Furans can undergo oxidative cleavage with MCPBA (Eq. 55). (653-655)



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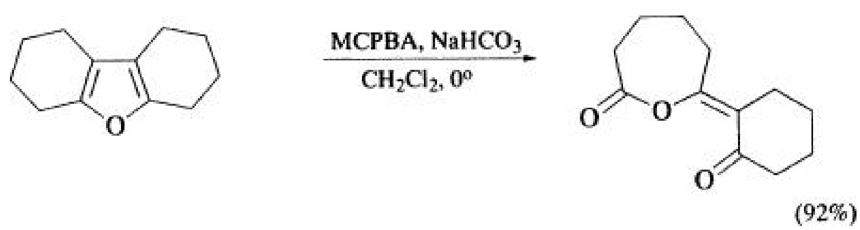
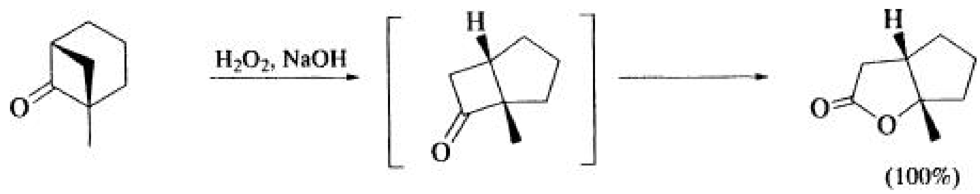


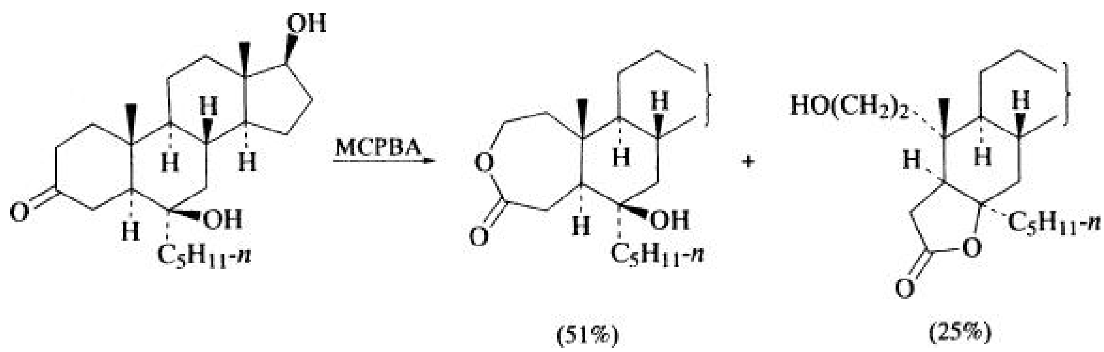
(55)

Baeyer–Villiger catalysts can epimerize (63, 154) or rearrange (226) ketone substrates. An example of structural rearrangement in basic hydrogen peroxide is shown in Eq. 56. (656) Sensitive functional groups may be altered. Silyl protecting groups



(56)

usually survive treatment with buffered peracids, but partial loss of *O-tert*-butyldimethylsilyl groups is reported; (53, 58) *O-tert*-butyldiphenylsilyl is more stable to peracid. (53) Acid-catalyzed ester exchange between the acid of the peracid and the product ester (58, 657, 658) is minimized by using a buffer such as disodium hydrogen phosphate, common in trifluoroperacetic acid oxidations. (15, 42) Intramolecular ester exchange of hydroxy lactones (355) (Eq. 57) (659) or dilactones (Eq. 58) (660) occurs even in



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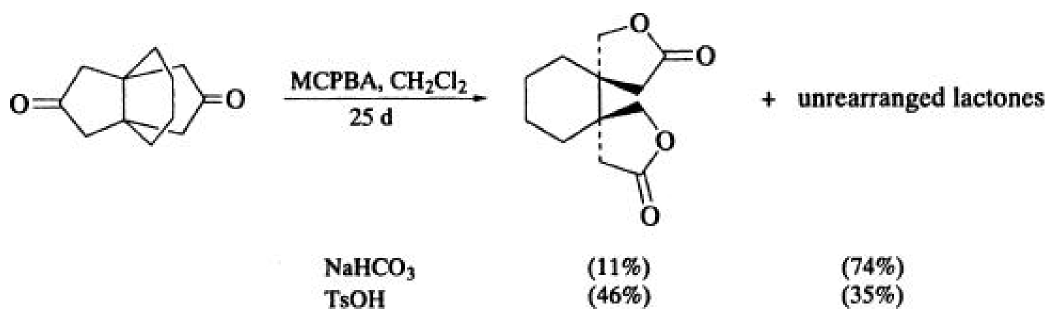
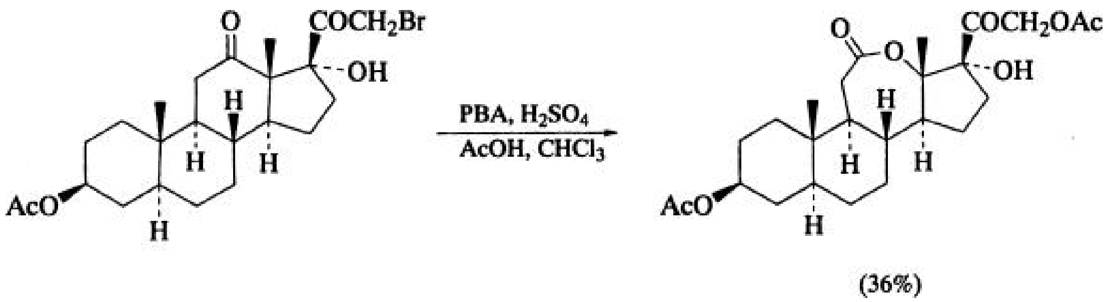


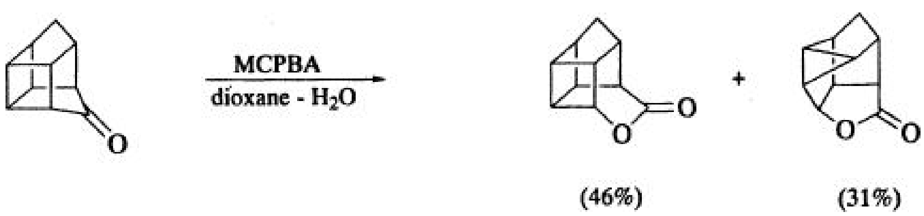
(58)

the presence of buffer, although acid catalysis accelerates the exchange. Lactone formation can follow the basic hydrolysis of an acetate ester. (63, 91, 661) Reactive halides may be converted to esters by displacement with acid nucleophiles (Eq. 59). (282)



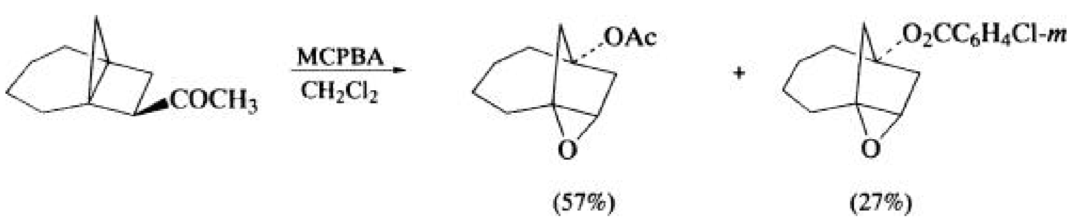
(59)

The combination of ring strain and acidic catalysts is conducive to formation of cationic rearrangement products from lactones. A commonly observed process upon oxidation of strained cyclobutyl ketones is rearrangement of the derived cyclobutanol ester (658, 662) or lactone (364, 379, 663, 664) to a cyclopropyl carbinyl isomer (Eq. 60). (377)



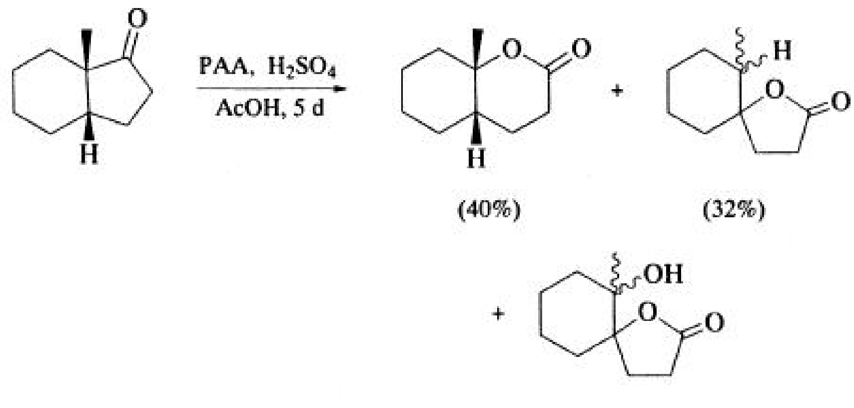
(60)

This process can occur even if the oxidation is carried out with buffered peracid. (658) The rearrangement of cyclopropylcarbinyl esters to 4-butenyl esters (52, 662, 665) can be accompanied by epoxidation of the double bond (Eq. 61). (657)



(61)

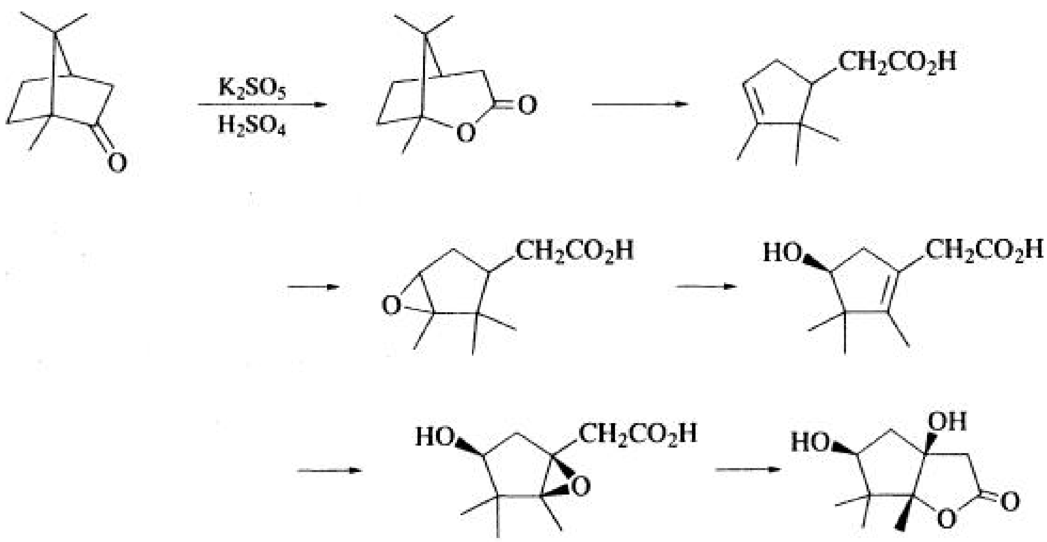
The combination of a strongly acidic reaction medium and the lactone or ester of a tertiary alcohol may generate a tertiary cation, which can behave in a number of ways. Alkyl shifts (440, 666) and hydride shifts (Eq. 62) (667) can afford rearranged lactones.



248 (28%)

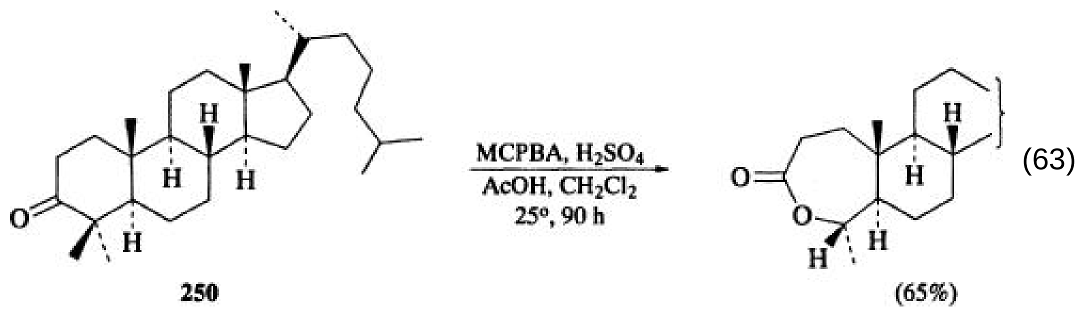
(62)

Olefins formed by proton loss from cations can be further oxidized by peracid; (667) hydroxylactones **248** (667) and **249**, (668) the latter a side product from camphor oxidation, are examples of rearranged and overoxidized Baeyer–Villiger products.

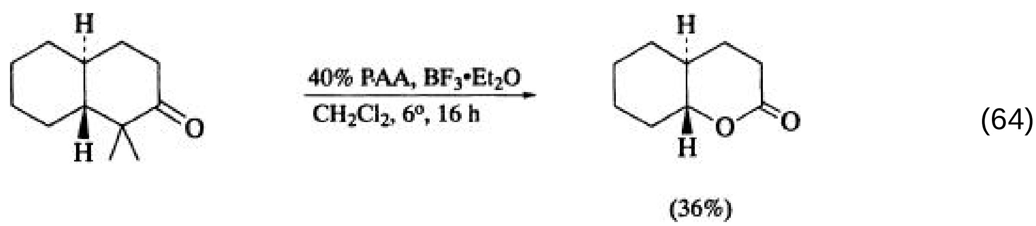


249 (10-15%)

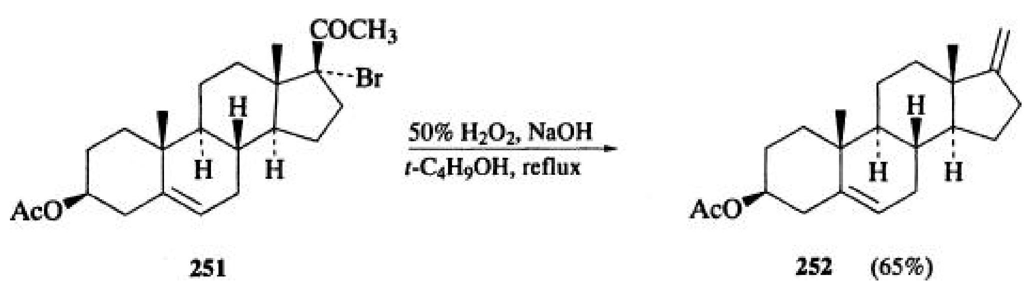
Oxidation of 4,4-dimethylcholestan-3-one (**250**) with MCPBA in the presence of 10% sulfuric acid/acetic acid results in loss of a methyl group (Eq. 63). (251, 669, 670) This



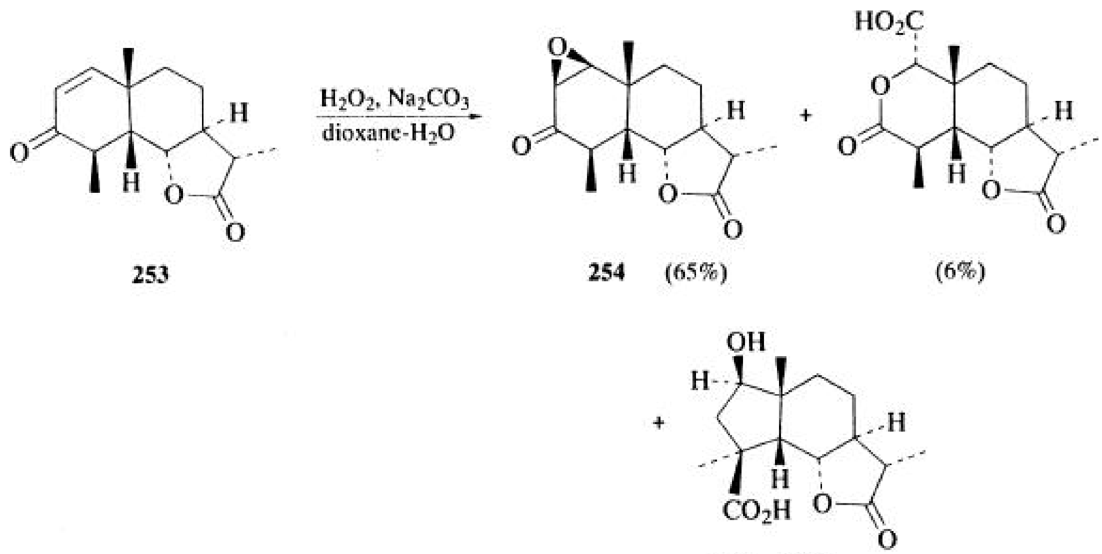
process, which involves acid-catalyzed ring opening, elimination, and further oxidations, has been modified with boron trifluoride and 40% peracetic acid into a synthetically useful procedure for “exhaustive” Baeyer–Villiger oxidations of α , α -dimethyl fused ring ketones to give lactones (Eq. 64). (284, 285, 622, 671) The latter are convertible to enones. (285)



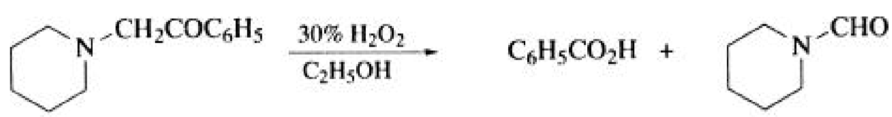
The α -bromoketone **251** reacts with basic hydrogen peroxide by a Favorskii process to give a cyclopropanone, which upon trapping with peroxide anion liberates carbon dioxide and olefin **252**. (672) A Favorskii rearrangement of the epoxyketone



254, during basic hydrogen peroxide oxidation of α , β -unsaturated ketone **253**, provides the ring contracted acid **255**. (673) Hydrogen peroxide causes oxidative fragmentation of α -*N,N*-dialkylaminoketones (Eq. 65). (73) Dunnione (**256**) is somehow fragmented and rearranged by basic hydrogen peroxide to give the diacid **257**. (674)

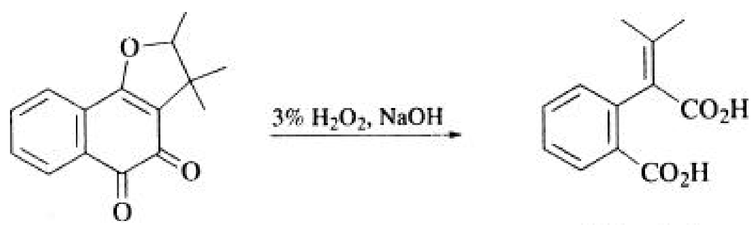


253 — 254 (65%) — (6%) — 255 (8%)



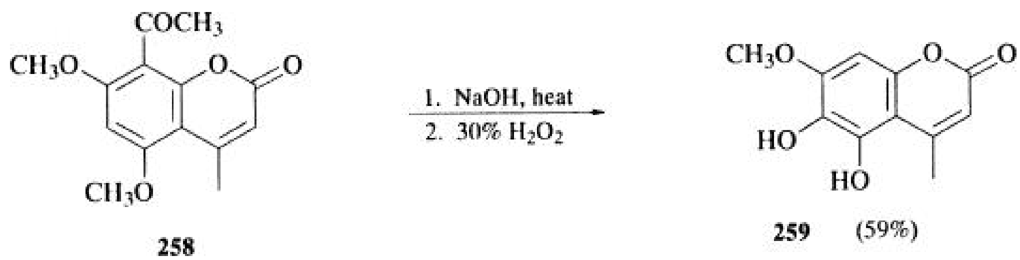
(94%) (14%)

(65)

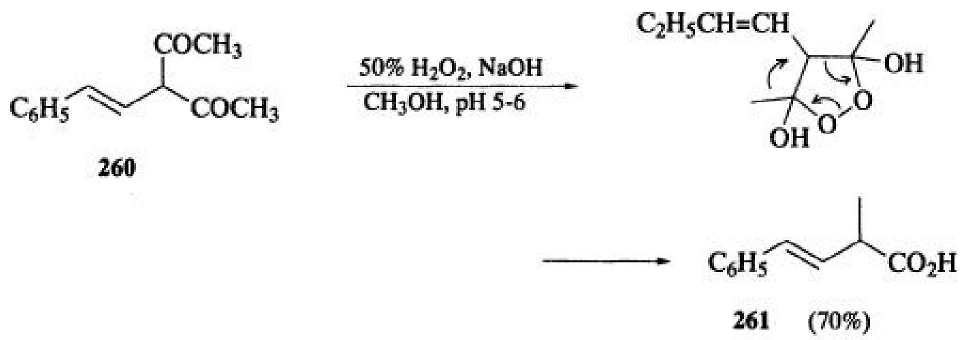


256 — 257 (—)

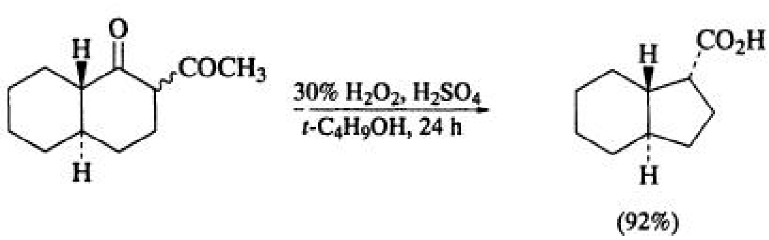
As discussed in the section on aldehyde oxidations, oxidation to a carboxylic acid can compete with the Baeyer–Villiger oxidation. (584) In the reaction of aryl aldehydes, a further side reaction in the Baeyer–Villiger oxidation is in situ hydrolysis of the formate ester to a phenol, which is further oxidized to a quinone [See Eq. 32]. (571, 572, 675) Less usual is selective demethylation of a methoxy group; the rearranged coumarin **259** is formed during the Dakin oxidation if the acetyl coumarin **258** is preheated with base to open the lactone ring to form a *trans*-cinnamic acid. (676)



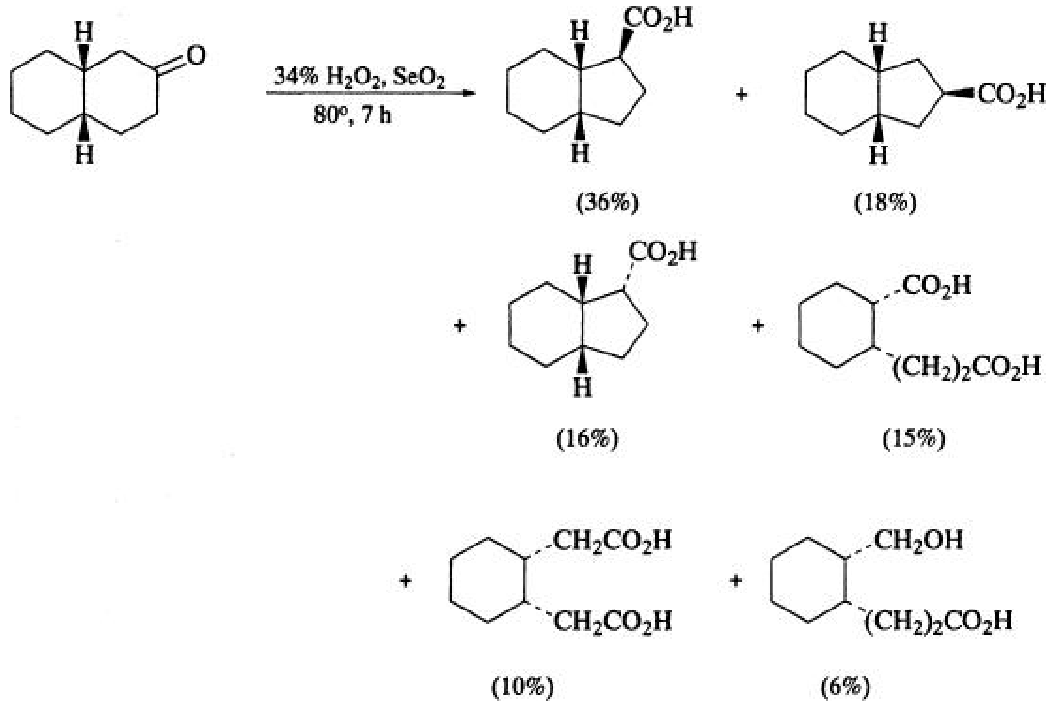
Rearrangement, rather than Baeyer–Villiger oxidation, of 1,3-diketone **260** to give acid **261** occurs with basic hydrogen peroxide. (677) Similarly, ring contraction of α -acyldecalones occurs upon treatment with acidic hydrogen peroxide (Eq. 66). (82)



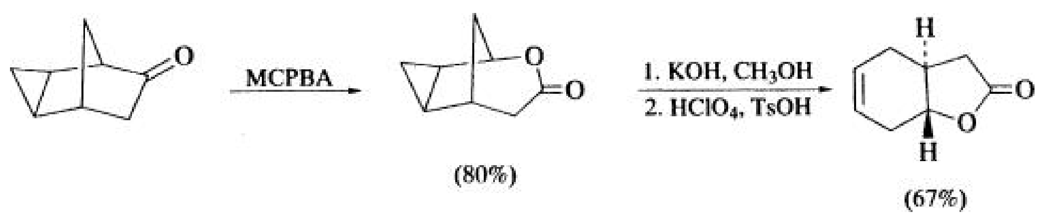
(66)



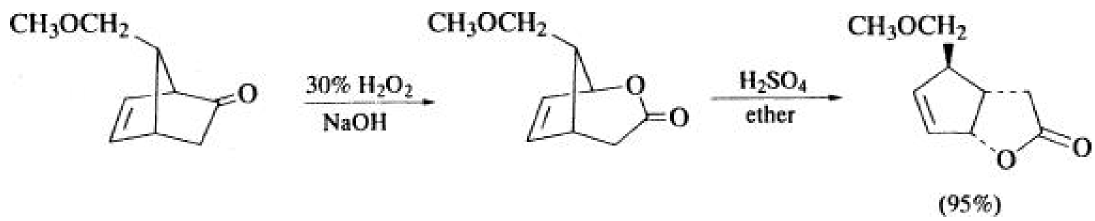
Cyclic ketones can be oxidized by hydrogen peroxide in the presence of selenium dioxide to give ring-contracted acids; these are accompanied by diacids and hydroxy acids derived by ring opening and further oxidation of the lactones formed by Baeyer–Villiger oxidation (Eq. 67). (678-680)


(67)

Rearrangements of Baeyer–Villiger products can be carried out during the reaction workup. The solvolysis of cyclopropyl carbinols prepared by the Baeyer–Villiger reaction has been developed into an efficient and stereoselective route to fused-ring γ -butyrolactones (Eq. 68). (422) Allylic rearrangement of bridged bicyclic lactones is

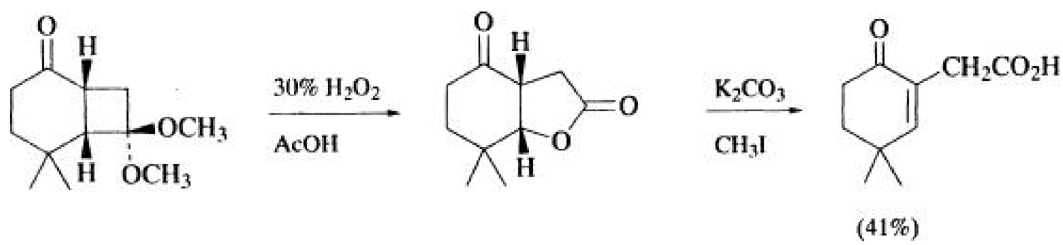

(68)

useful in the stereocontrolled synthesis of substituted cyclopentenes (60, 414-416, 681) and cyclohexenes. (423) The acid-catalyzed rearrangement, although useful in the synthesis of prostaglandin precursors (Eq. 69), (395, 681) can be avoided if the lactone is opened



(69)

with base and the carboxylate anion is converted to the ester. (389) Lactones of β -hydroxycyclohexanones are converted to substituted cyclohexenones upon treatment with sodium hydroxide; (423) the reaction is part of a method for α -carbalkoxymethylation of α , β -unsaturated ketones nonenolizable toward the γ position (Eq. 70). (111)



(70)

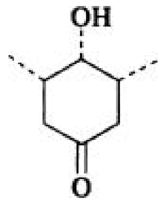
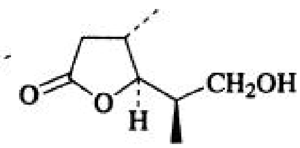
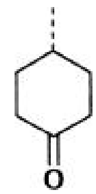
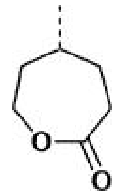
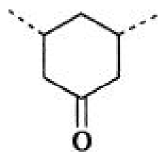
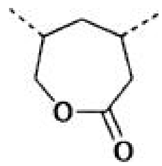
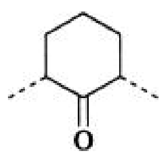
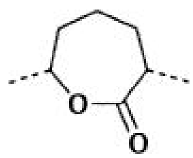
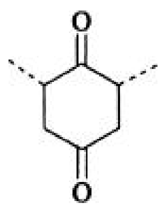
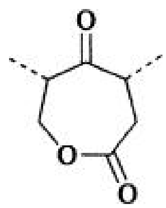
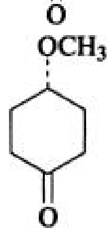
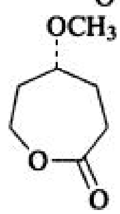
3.12. Alternative Methods

3.12.1.1. Biological Methods

Although the biological Baeyer–Villiger oxidation is not included in the tabular portion of this review, microorganisms are capable of converting ketones to lactones. (172, 682-684) Enantioselective enzymatic conversions of mesomeric cyclohexanones to lactones with cyclohexanone monooxygenase (EC 1.14.13.-) are shown in Table 7. (685) The enzyme is extremely efficient at discriminating between the two sides of the carbonyl group. The analogous enantioselective Baeyer–Villiger reaction using chemical rather than biological chiral reagents has not been reported.

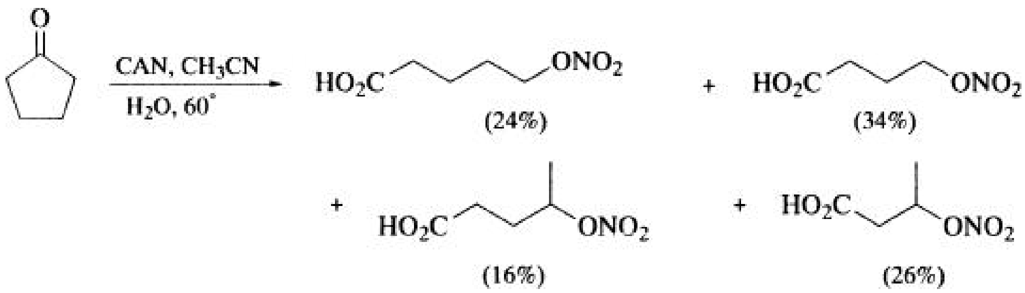
Table 7. Enzymatic Oxidation of Selected *meso*-Cyclohexanones

Substrate	Product	Yield (%)	ee (%)

		88	>98
		80	>98
		73	>98
		27	>98
		25	>98
		76	75

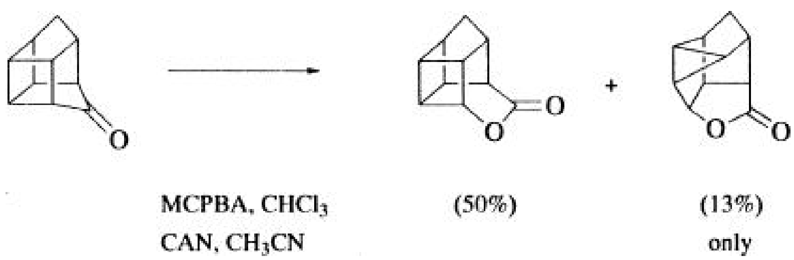
3.12.1.2. Non-Peracid Oxidants

The Baeyer–Villiger reaction is normally defined as the conversion of a ketone to a lactone with a peracid or other peroxy compound. The same transformation to lactones or related cleavage products can be effected using other oxidizing agents. Ceric ammonium nitrate (CAN) cleaves cyclopentanones and cyclohexanones; however, the reactions can be accompanied by rearrangements and chain shortening (Eq. 71). (686) Bridged ketones in which the carbonyl is part of a

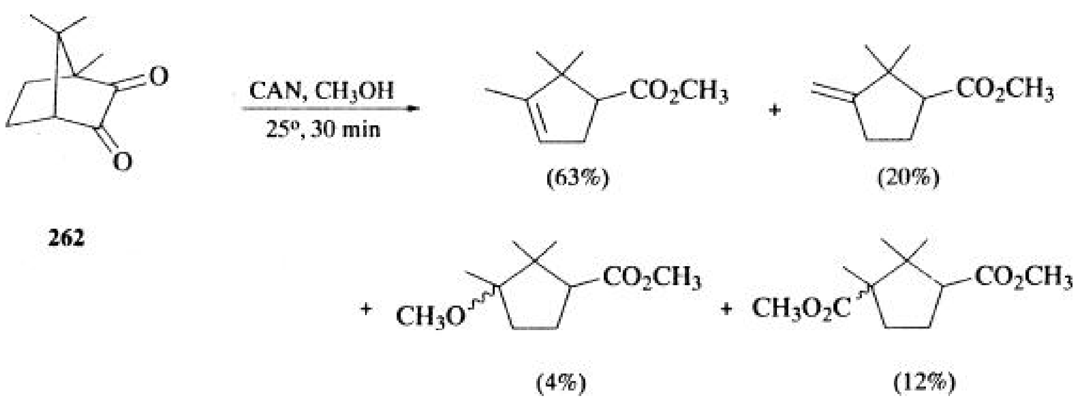


(71)

strained ring can be oxidized to lactones with ceric ammonium nitrate in acetonitrile, (378, 380, 687-689) or lead tetraacetate in pyridine/benzene; (377, 690) however, rearrangements are more prevalent with these oxidants than during Baeyer–Villiger oxidations with MCPBA (Eq. 72) (380) Bridged 1,2-diketone **262** reacts with ceric ammonium nitrate to form a mixture of products. (691)

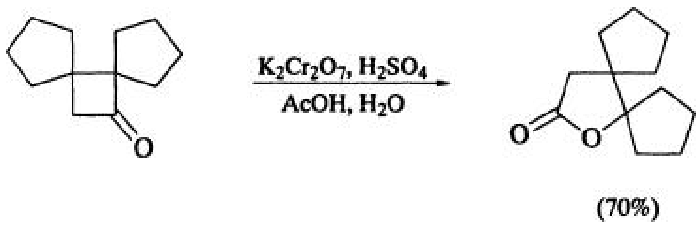


(72)



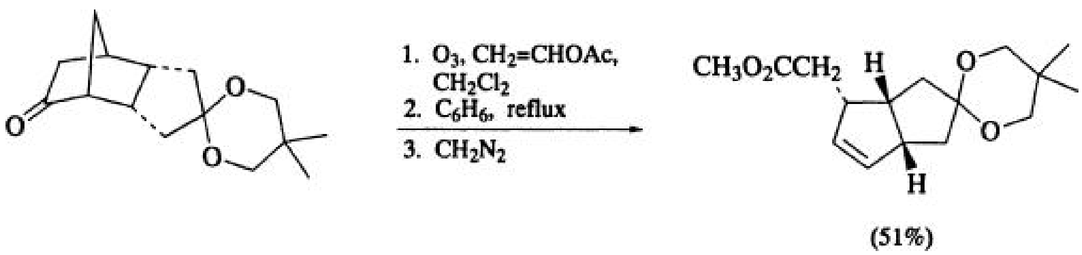
262

Chromic acid oxidation of cyclobutanones flanked by a secondary or tertiary alkyl group leads to butyrolactones; (692-695) an example is shown in Eq. 73. (694)

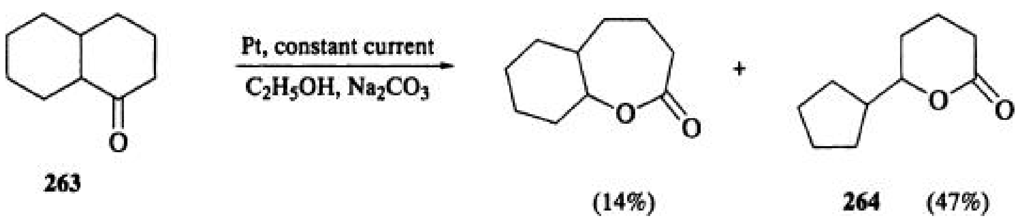


(73)

Ozonolysis of vinyl acetate generates formaldehyde oxide ($CH_2 = O^+ - O^-$), which reacts with ketones to give lactones or related cleavage products (Eq. 74). (696) Anodic oxidation of ketone **263** affords mainly rearranged lactone **264**. (697)

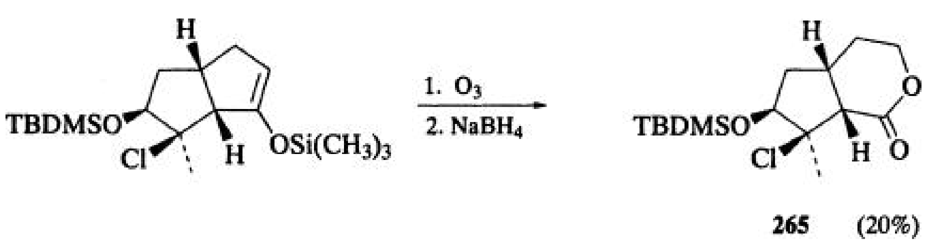


(74)



3.12.1.3. Oxidation of Ketone Derivatives

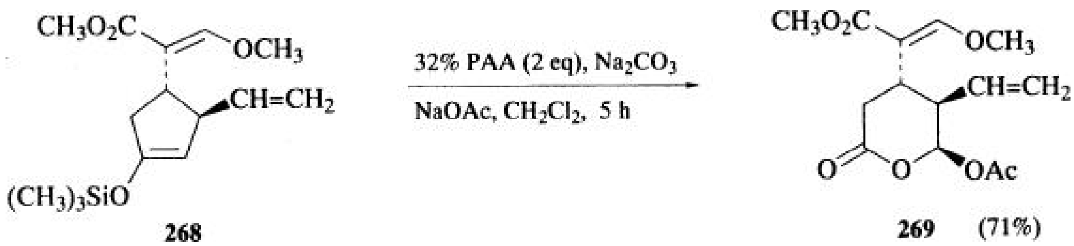
Enolsilanes, which can be prepared with regiocontrol, (698, 699) form lactones following reductive workup of the product of ozonolysis. This method is complementary to the Baeyer–Villiger reaction in that it allows oxygen to be introduced at the less substituted carbon. (698, 700) The utility of the method in the preparation of lactone **265** is shown in Eq. 75. Baeyer–Villiger oxidation



(75)

of fused ketone **266** with MCPBA favors bridgehead migration and affords an 80:20 mixture of lactones **267** and **265**. (701)

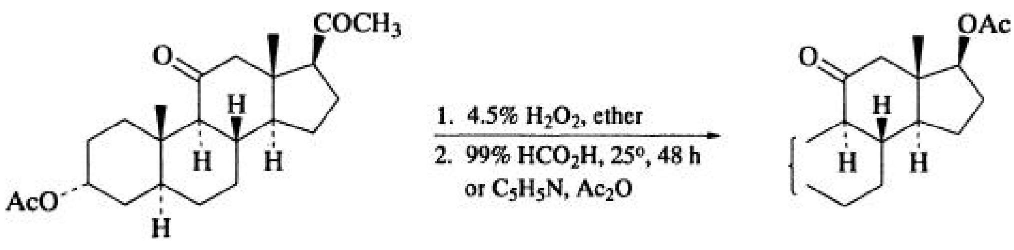
Epoxidation of enol silanes followed by rearrangement leads to α -acyloxyketones, which are subject to Baeyer–Villiger oxidation. Treatment of enol silane **268** with excess peracetic acid yields in chemoselective and regioselective fashion the acetoxylactone **269**. (702)



Methyl ketones generally undergo a two-carbon chain shortening to give acetate esters under Baeyer–Villiger conditions; however, formation of a terminal enol silane and ozonolysis converts a methyl ketone to a carboxylic acid of one less carbon. (698) Enol acetates can be used in place of enol silanes. (703) Fused enol ethers (704-712) and fused furans (713) can be cleaved to ketolactones with MCPBA (Eq. 76). (704)

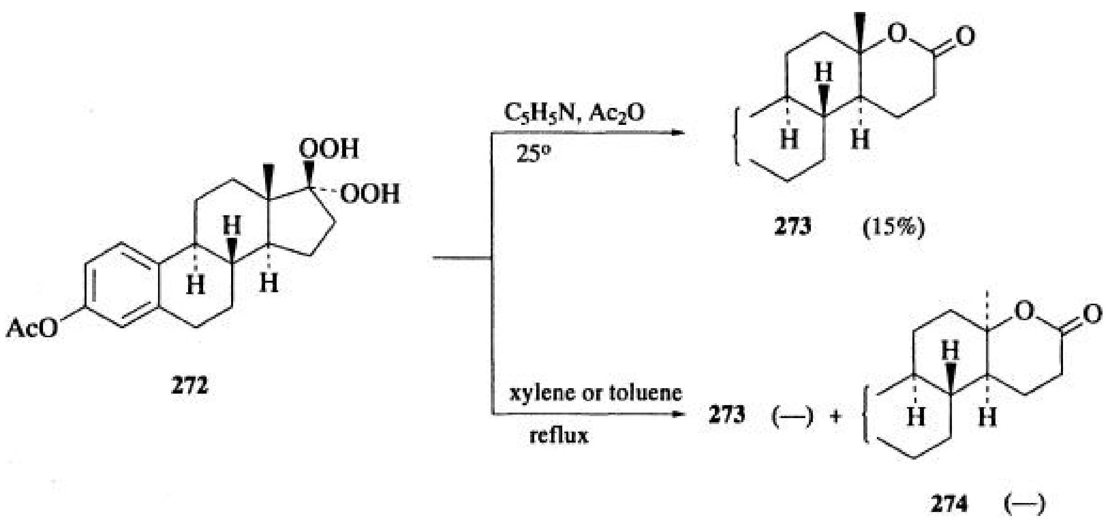
(76)

A reaction which is similar to the Baeyer–Villiger oxidation is the reaction of ketones with ethereal 4–8% hydrogen peroxide and subsequent rearrangement of the bis-hydroperoxide adducts to lactones by pyrolysis in refluxing solvent, (714) or treatment with anhydrides (714, 715) or acids. (716) By this method the C-20 ketone **270** is converted chemoselectively to the 17-acetoxysteroid **271**. (715, 716) Epimerization at C-13

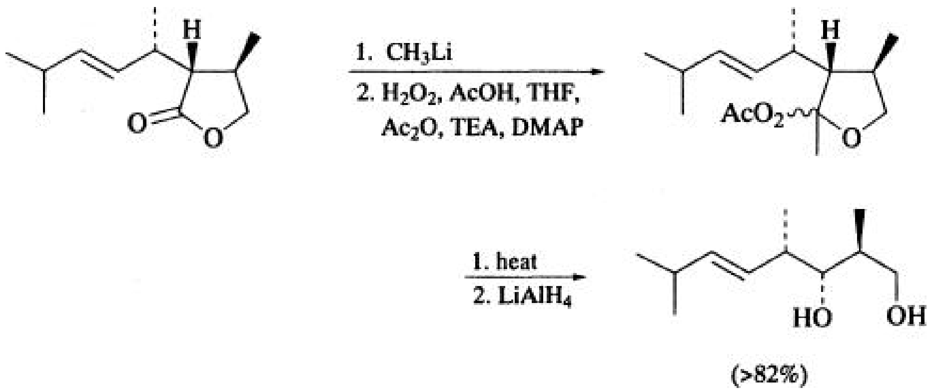


270 **271** (15%)

occurs when the bis-peroxide **272** is converted to lactones **273** and **274** by refluxing in xylene or toluene. (714)

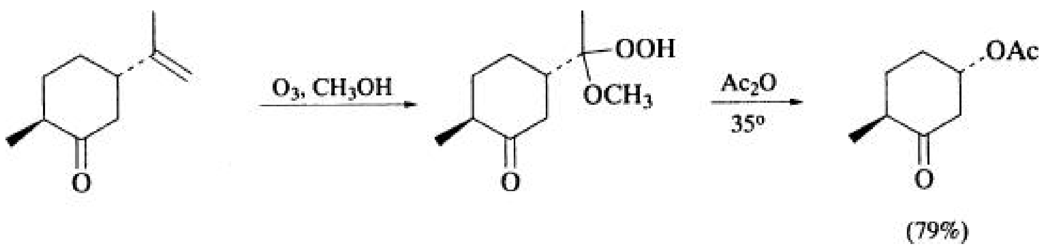


Related to the rearrangement of bis-hydroperoxides is the rearrangement sequence of lactones to diols shown in Eq. 77. (717-719) Rearrangement of the acylated α -alkoxy

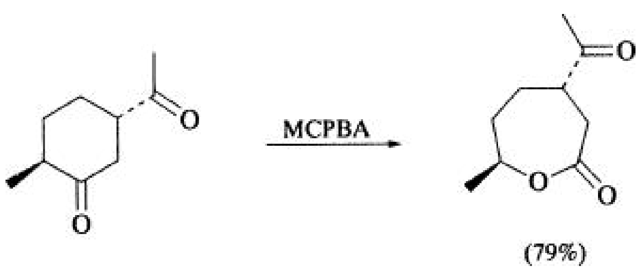


(77)

hydroperoxide is effected by heating. (720) Since α -alkoxyhydroperoxides can be formed by ozonolysis of olefins, the method of Eq. 78 can be a useful complement to the Baeyer–Villiger oxidation in Eq. 79. (110)

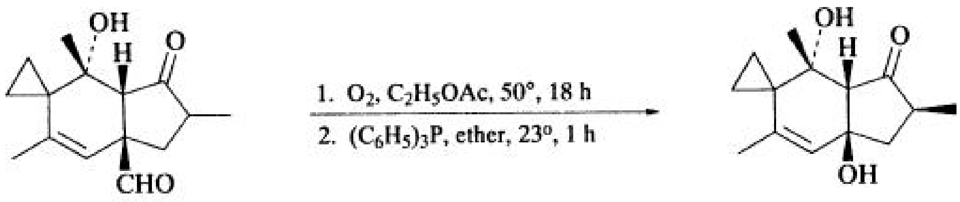


(78)



(79)

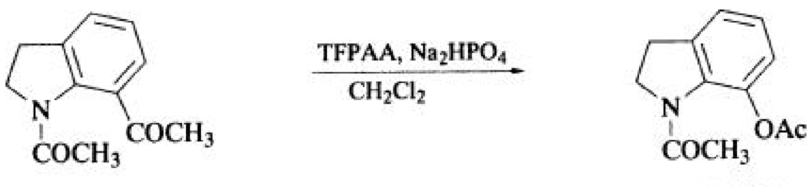
A mild chemoselective method for oxidative deformylation involves conversion of an aldehyde to a hydroperoxide with oxygen, followed by rearrangement and subsequent reduction. (721) This method was useful for a chemoselective oxidation of the sensitive substrate **275**. (721)



275

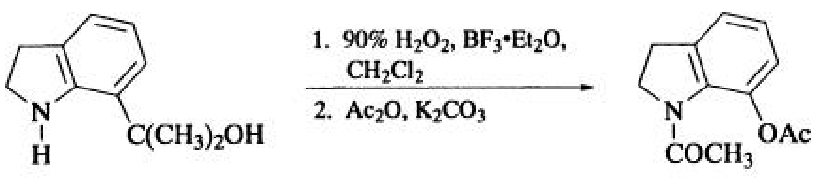
(37%)

Baeyer–Villiger oxidation of highly electron-rich acetophenones with one or two groups *ortho* to acetyl often is difficult with peracids (Eq. 80). In such cases



(80)

phenols often can be prepared by rearrangement of secondary or tertiary benzylic hydroperoxides, which can be derived from the corresponding acetophenone or benzoate ester (Eq. 81). (722, 723) The method also is useful for aromatic substrates, such as

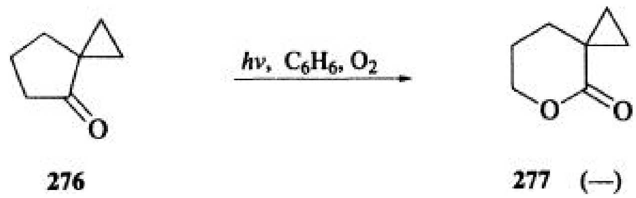


(81)

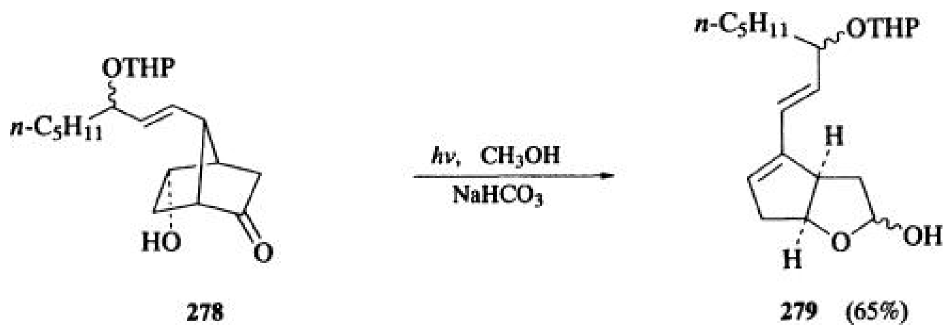
indolines, which undergo secondary reactions at the expense of the Baeyer–Villiger reaction.

3.12.1.4. Photochemical Methods

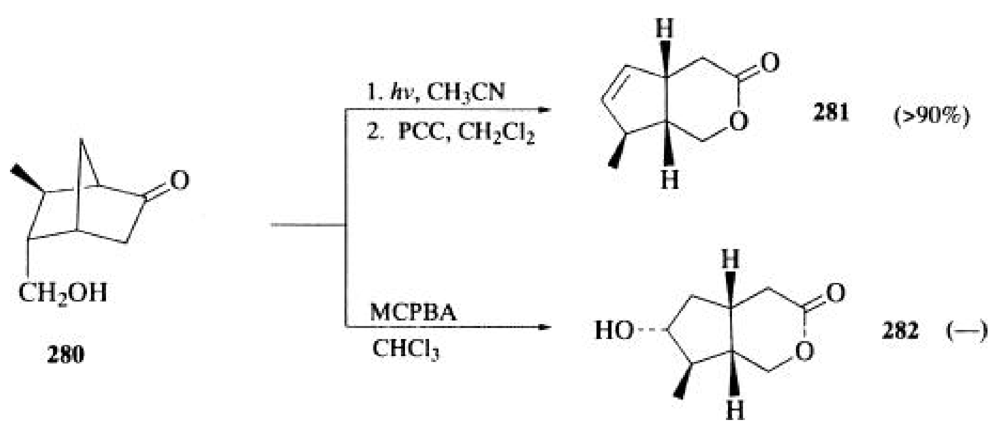
If certain structural requirements are met, it is possible to expand cyclic ketone rings photochemically to hemiacetals, which can be oxidized to lactones. (350, 724-727) Photochemical oxidative expansions of cyclobutanones are aided by α substitution, and insertion of oxygen occurs with retention of stereochemistry at the migrating center. (229, 724, 728) Irradiation of spirocyclopentanone **276** in the presence of oxygen gives lactone **277**. (724) The method provides lactones



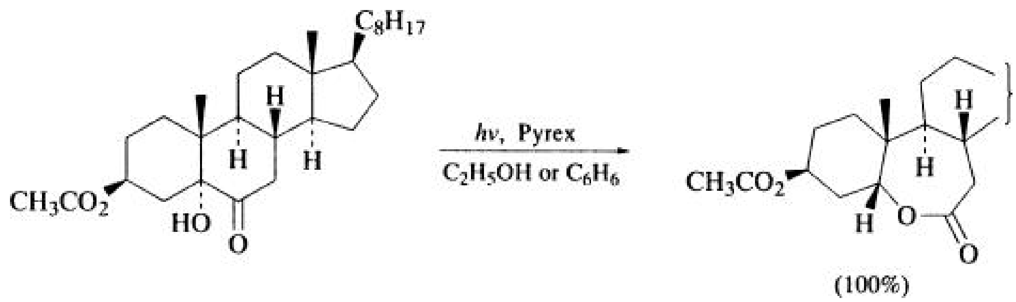
from several 3-oxacyclopentanones and 3-oxacyclohexanones and some bicyclo[2.2.1]heptanon-2-ones. (724) An example of the latter is the rearrangement of bridged ketone **278** to give the lactol **279**. (350) Norrish type I reaction of bridged



ketone **280** followed by oxidation is an alternative to Baeyer–Villiger reaction for the synthesis of the structurally similar lactones **281** and **282**. (355) Although other simple

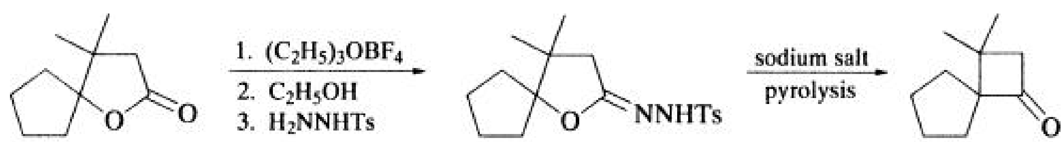


cyclopentanones and cyclohexanones do not give lactones, irradiation of an α-hydroxy-6-ketosteroid can result in stereospecific rearrangement to a lactone (Eq. 82). (310)



(82)

Mechanistically related to the photochemical ring expansion of ketones to hemiacetals is the thermal decomposition of lactone tosylhydrazones (Eq. 83). The reaction sequence from lactone **283** to ketone **284** is formally a retro Baeyer–Villiger oxidation. (729)



(83)

283

284 (42%)

4. Experimental Considerations

4.1. Reagents and Conditions

This section describes the preparation and handling of the most frequently used Baeyer–Villiger reagents. At the time of the earlier review of this reaction hydrogen peroxide, permono- and perdisulfuric acid, peracetic acid, perbenzoic acid, and monoperphthalic acid were commonly used as reagents. (2) Since then, two commonly used oxidants have been TFPAA (90%), a powerful oxidant customarily prepared as needed from 90% hydrogen peroxide, and *m*-chloroperbenzoic acid (85%), a stable solid also prepared from 90% hydrogen peroxide. Unfortunately, problems associated with the use and transportation of 90% hydrogen peroxide, which is highly explosive. (730, 731) have eliminated the commercial availability of reagents based upon this oxidant. If necessary, 90% hydrogen peroxide can be prepared by concentration of 30% hydrogen peroxide, (732) or substitution of commercially available 70% hydrogen peroxide (FMC Peroxygen Chemicals Division, Philadelphia, PA) might be attempted. In the alternative, judicious use of the information in this review concerning peracid purification procedures, alternative oxidants, catalysts, and radical scavengers which allow use of higher temperatures, should mitigate the loss of commercial reagents based upon 90% hydrogen peroxide.

In all peroxide oxidations of new compounds the possibility of reactions occurring with explosive violence must be considered. (2) *When tetrahydropyranyl ether derivatives were treated with alkaline hydrogen peroxide or 40% peracetic acid followed by washing with 10% sodium sulfite solution, attempted distillation led to detonation without prior warning.* (733)

Among the factors that go into choosing a peracid is its reactivity. The oxidizing power of a peracid is related to the strength of the conjugate acid of its leaving group; so the reactivity order of some commonly used peracids is TFPAA > monopermaleic acid, (349) > mono-*o*-perphthalic acid, (349) > 3,5-dinitroperbenzoic acid, (734) > *p*-nitroperbenzoic acid (424) > MCPBA = performic acid, (349) > perbenzoic acid > peracetic acid ≥ hydrogen peroxide > *tert*-butyl peroxide. (7)

4.1.1.1. Trifluoroperacetic Acid (90%)

TFPAA (90%) is prepared prior to use by adding trifluoroacetic anhydride or trifluoroacetic acid (735) to a suspension of 90% hydrogen peroxide in methylene chloride at 0°. (3, 7, 42) Oxidations usually are performed in methylene chloride in the presence of a suspension of disodium hydrogen phosphate buffer, which usually eliminates transesterification as a side reaction. An example of a reaction is known which proceeds faster in the presence of 1 equivalent of buffer than 2 or more equivalents; (79) another reaction has been found to proceed better if the surface of a Teflon or Pyrex flask was virgin and not etched. (731) Typical reaction temperatures range from 0° to reflux, and reaction times are from a few minutes to several hours. There is no loss of active oxygen by TFPAA (90%) after 24 hours at reflux. (735) The TFPAA solutions prepared from 30% hydrogen peroxide have been used effectively; (736) but reactions are slowed. (735)

4.1.1.2. Nitroperbenzoic Acids

Crystalline 3,5-dinitroperbenzoic acid is prepared from 90% hydrogen peroxide and 3,5-dinitrobenzoic acid in methanesulfonic acid. (734) Oxidation of unreactive substrates can be performed by refluxing with this reactive oxidant in halogenated solvents for several hours in the presence of a radical scavenger, 4,4¢-thiobis(6-*tert*-butyl-3-methylphenol). The reagent is comparable in strength to TFPAA (90%), except that no buffers are needed. (734)

p-Nitroperbenzoic Acid (PNPBA) is a commercially available (Aldrich) crystalline solid, which can be prepared from *p*-nitrobenzoic acid and 94% hydrogen peroxide. (737-739) Oxidations are performed in halogenated solvents in the presence of a buffer, such as sodium bicarbonate. (424) The problems in manufacture from concentrated hydrogen peroxide may eliminate this peracid from commerce.

4.1.1.3. m-Chloroperbenzoic Acid (85%)

Oxidations with commercially available MCPBA (85%) generally are performed in chlorinated solvents at room temperature for several hours to several days. Some MCPBA oxidations proceed rapidly and in high yields when mixed in the solid state or when stirred in the presence of water, even though the ketone and MCPBA may be substantially insoluble. (740, 741) Oxidation can be effected at 55° in 1,2-dichloroethane if a radical scavenger, such as 2,4,6-tri(*tert*-butyl)phenol, is added. (446) Common buffers utilized include sodium hydrogen phosphate, sodium acetate, and sodium bicarbonate. Catalysis can be effected with either buffer (227) or acids; such as trifluoroacetic acid, (742) methanesulfonic acid, (431) sulfuric acid, (323) or Nafion-H (DuPont), a perfluorinated resin sulfonic acid. (323) MCPBA (99+%) can be prepared from lower strength peracid by washing with phosphate buffer of pH 7.5. (743) MCPBA is exceptionally stable and decomposes less than 1% after 1 year at room temperature. (743) Although widely used formerly, MCPBA (85%) is no longer commercially available. Weaker solutions of MCPBA are available from various vendors. (See monoperoxyphthalic acid, magnesium salt, below.)

4.1.1.4. Monopermaleic acid

MPMA (30%) can be prepared by dissolving maleic acid in dimethylformamide, adding 30% hydrogen peroxide and stirring at 25° for several hours. (349) A solution of MPMA (30%) in methylene chloride is prepared by reacting 30% hydrogen peroxide and acetic anhydride in methylene chloride and then adding maleic anhydride. (744) MPMA (90%) is prepared by adding finely crushed maleic anhydride to 90% hydrogen peroxide in methylene chloride at 0°. (44, 52) Oxidations are performed in methylene chloride at 25° or at reflux for 1–12 hours. Reactions are nearly as fast as those with TFPAA and no buffer is required. Permaleic acid solutions decompose to the extent of 5% in 6 hours at ambient temperature. (44)

4.1.1.5. Monoperphthalic Acid

The preparation of this acid has been discussed in *Organic Reactions*; (2, 349, 745) a modified procedure involves stirring finely powdered phthalic anhydride with 30% hydrogen peroxide in ether for 24 hours at 25°. (746) A 10% solution of monoperphthalic acid in ether at 3° for 30 days successfully oxidized a hindered acyl group to acetate after MCPBA, perbenzoic acid, and peracetic acid failed. (747)

4.1.1.6. Monoperphthalic Acid Magnesium Salt

Although little has been reported on use of MMPP to perform Baeyer–Villiger oxidations, this peracid is touted as a replacement for MCPBA (85%). (748) MMPP is a non-shock-sensitive crystalline solid, comparable in solid state stability to MCPBA, which contains about 80% of the pure oxidant as its hexahydrate. Baeyer–Villiger oxidations are performed in dimethylformamide or methanol–water at 20–30° for 4–16 hours. (748) The oxidation byproduct, magnesium phthalate, is water soluble.

4.1.1.7. Persulfuric Acid

Preparation of this acid has been discussed in *Organic Reactions*. (2) Oxidations can be carried out in aqueous solutions of persulfuric acid, (541, 749, 750) and in methanol–sulfuric acid mixtures. (41) A stable mixture of potassium peroxymonosulfate, potassium hydrogen sulfate, and potassium sulfate has been described. (574)

4.1.1.8. Performic Acid

Preparation of this acid has been discussed in *Organic Reactions*. (745) Oxidations can be performed by adding 30% hydrogen peroxide to a solution of the substrate in formic acid (349) or in a buffered mixture of formic acid in methylene chloride. (616)

4.1.1.9. Peracetic Acid

Details of the preparation and titration of this acid are given in *Organic Reactions*. (2, 745) Solutions containing approximately 40% peracetic acid are commercially available (Aldrich). Solutions of peracetic acid can be prepared by adding 90% hydrogen peroxide to a mixture of sulfuric acid and acetic anhydride (751, 752) or 30% hydrogen peroxide to 90% aqueous acetic acid.

(237) Oxidations are customarily performed in glacial acetic acid in the presence of sodium acetate. (349, 424, 753) Solutions of peracetic acid in acetone or ethyl acetate are used. (754) In a non-Baeyer–Villiger process the oxidizing effectiveness of a mixture of 30% hydrogen peroxide, acetic anhydride, and sulfuric acid is comparable to that reported for 90% hydrogen peroxide in an acetic acid/sulfuric acid mixture. (755)

4.1.1.10. Perbenzoic Acid

Details of the preparation of this acid are given in *Organic Reactions*. (2, 745) Reactions are normally performed in chloroform, methylene chloride, or carbon tetrachloride; *p*-toluenesulfonic acid is often used as an acid catalyst. (306)

4.1.1.11. Hydrogen Peroxide–Base Catalysis

Use of basic hydrogen peroxide in Baeyer–Villiger and Dakin oxidations has been discussed in *Organic Reactions*. (2) Typically 6% hydrogen peroxide and 2 N sodium hydroxide are heated at 40–60° with the aldehyde for 1–12 hours. (545, 549) Baeyer–Villiger oxidations of cyclobutanones and bicyclo[2.2.1]hepten-2-ones are effected using a mixture of aqueous 30% hydrogen peroxide and 10% sodium hydroxide in methanol or methanol–tetrahydrofuran. (190, 195, 397, 415)

4.1.1.12. Hydrogen Peroxide–Acid Catalysis

Sulfuric acid catalyzes oxidation of electron-rich benzaldehydes with 31% hydrogen peroxide in methanol to give phenols. (579, 611) Nafion-H (DuPont), a resin sulfonic acid, catalyzes the Baeyer–Villiger oxidation of cyclopentanones and cyclohexanones with 30% hydrogen peroxide in methylene chloride. Reactions are performed at reflux temperature for 1–36 hours. (323) Cyclobutanones react to give lactones with 30% hydrogen peroxide in the presence of 2,2,2-trifluoroethanol, acetic acid, potassium hydrogen sulfate–methanol, ethanol, or acetonitrile. (756)

4.1.1.13. Alkyl Hydroperoxides–Base Catalysis

Cyclobutanones can be selectively oxidized in the presence of olefins and larger rings with commercially available [Aldrich] *tert*-butyl hydroperoxide and 10% sodium hydroxide in tetrahydrofuran. (272) Simple aliphatic ketones are oxidized to esters with 90% hydrogen peroxide and boron trifluoride etherate at room temperature. (46) Triphenylmethyl hydroperoxide–sodium hydroxide and 10% sodium hydroxide have been used in a similar manner for chemoselective cyclobutanone oxidation. (249, 250)

4.1.1.14. Silylated Peracids

Silylated forms of hydrogen peroxide and persulfuric acid can be prepared from hydrogen peroxide. (757) Triphenylsilyl hydroperoxide behaves similarly to peracids with ketones on contact with basic alumina. (758) Bis(trimethylsilyl) peroxide (521) reacts with ketones in methylene chloride under the influence of trimethylsilyl trifluoromethanesulfonate, (221) stannic chloride, (220) or boron trifluoride etherate as catalysts. (220, 477) Olefins are not attacked.

Bis(trimethylsilyl) monoperoxysulfate is prepared from bis(trimethylsilyl) peroxide. Unlike persulfuric acid, the silylated reagent is soluble in nonprotic and nonpolar media such as methylene chloride. (36, 47) The reagent has general scope; however, it attacks olefins, and lactones may hydrolyze.

4.1.1.15. Benzeneperoxyseleninic Acids

Benzeneperoxyseleninic acid is generated in situ upon adding 30–90% hydrogen peroxide to benzeneseleninic acid or diphenyldiselenide in methylene chloride, tetrahydrofuran, or chloroform. (222, 578, 600, 628) A phosphate buffer has been used. (222) Reaction times vary from an hour to several days at 25–40°. The reagent prepared using 30% hydrogen peroxide has proven successful when 40% peracetic acid and 85% MCPBA have failed. (222) More powerful oxidants prepared from the corresponding diselenides or seleninic acids include *o*-nitrobenzeneperoxyseleninic acid and 2,4-dinitrobenzeneperoxyseleninic acid. (578, 600, 628) These oxidants are expecially efficient for conversion of aryl aldehydes and ketones into phenols, (578) and for oxidation of α , β -unsaturated aldehydes to vinyl formates. (600, 628)

4.1.1.16. Sodium Perborate

Sodium perborate is a cheap, large-scale industrial chemical. It is used for the Baeyer–Villiger oxidation of diaryl, arylalkyl, and cyclic ketones in either trifluoroacetic acid or acetic acid/trifluoroacetic acid mixtures at temperatures of 25–60° for 4–8 hours. (114)

4.1.1.17. Resin-Bound Peracids

Polystyrene-bound phenylseleninic acid is readily prepared from polystyrene. (43) Oxidations are effected by stirring a slurry of the ketone in methylene chloride with the resin and 30% hydrogen peroxide. Less water-soluble ketones are unreactive and appreciably water-soluble products undergo hydrolysis. The polymer can be reused, but it is destroyed by forcing conditions.

Arsenated polystyrene resins catalyze diphasic and triphasic Baeyer–Villiger oxidations of ketones in methanol, dioxane, or chloroform with 30% or 90% hydrogen peroxide at 80°. In water-miscible solvents, medium-size cycloalkanones, steroidal ketones, and branched-chain aliphatic ketones are oxidized. (182) Advantages of the reusable resins are their ease of separation from the reaction, low or no protic or Lewis acid activity, and the low cost and convenience of hydrogen peroxide, which gives water as its byproduct.

Polystyrene carboxylic acids catalyze epoxidations. (759) There are no reports found of their use in Baeyer–Villiger oxidations.

4.1.1.18. Uncommon Oxidants

Sparsely used Baeyer–Villiger reagents which have no reported advantage over more commonly used oxidants include *o*-sulfoperbenzoic acid in aqueous acetone, (760) *p*-carbomethoxyperbenzoic acid in chloroform, (761) *N*- β , β , β -trichloroethoxycarbonylperoxycarbamic acid (30%) in methylene chloride, (102, 230) and *N*-benzoylperoxycarbamic acid (92%) in tetrahydrofuran. (102) Molybdenum peroxo complexes stabilized by picolinato and pyridine-2,6-dicarboxylato ligands catalyze oxidation of cyclic ketones by 90% hydrogen peroxide, but yields are poor. (762, 763) Permonophosphoric acid, prepared from 90% hydrogen peroxide and phosphorus pentoxide, oxidizes acetophenones. (28) Effective permonophosphoric oxidations can be performed using 70% hydrogen peroxide; advantages in cost and rate of Baeyer–Villiger rearrangements under easy to run conditions should result in increased use of this peracid as commercial oxidants based upon 90% hydrogen peroxide become unavailable. Inexpensive and commercially available sodium percarbonate in trifluoroacetic acid conveniently and under mild conditions oxidizes aryl and cycloalkyl ketones to esters. (763a)

4.2. The Apparatus

For most reactions it is convenient to use a three-necked, round-bottomed flask equipped with an appropriately sized mechanical stirrer, and, if necessary a thermometer and dropping funnel. In some cases a drying tube may cap the reflux condenser or a gas inlet tube may be used to introduce nitrogen (549) or argon. (764) If long reaction times are anticipated, reactions may be run in the dark to minimize decomposition of the peracid reagent.

4.3. The Workup Procedure

For reactions performed in organic solvents, unreacted peracids generally are decomposed by addition of solutions of sodium bisulfite, sodium thiosulfate, or sodium sulfite. (334, 349, 415, 578) Washing may be continued until a negative starch–iodide test is observed. (445) Insoluble resins and acids formed by decomposition of peracids are removed by filtration. Soluble acids are removed by washing with 10% solutions of sodium bicarbonate or sodium carbonate. Peracids are also removed by washing with these base solutions.

For reactions performed in nonorganic solvents with water-soluble peracids or aqueous hydrogen peroxide, the product is filtered if water insoluble (541) or taken up in an organic solvent, which is then treated as usual. (272)

4.3.1.1. Selection of Reaction Conditions

There is no evidence that alternative methods of introducing reactants (normal or inverse addition) has an effect on the yield of the Baeyer–Villiger oxidation.

For sluggish reactions, it is often advantageous to add additional aliquots of peracid at regular intervals. Use of a buffer, such as sodium acetate, disodium hydrogen phosphate, or sodium bicarbonate, or avoidance of strong acid catalysts will minimize ester exchange and hydrolysis of the esters or lactones. Weaker peracids, such as peracetic acid, generally are more regioselective than stronger peracids, such as MCPBA. (349, 424) A search for analogies in the tabular survey may facilitate the choice of the appropriate experimental conditions.

5. Experimental Procedures

5.1.1.1. (2R,3S,22R,23R)-2,3,22,23-Tetrahydroxy-B-homo-7a-oxa-5 α -ergostan-7-one Tetraacetate (Regioselective Oxidation of a Fused-Ring Ketone with 30% Trifluoroperacetic Acid) (736)

To a solution of trifluoroperacetic acid in dichloromethane prepared by adding trifluoroacetic anhydride (3.37 mL) to 30% aqueous hydrogen peroxide (0.6 mL) in dichloromethane (3.7 mL) at 0° was added (2*R*, 3*S*, 22*R*, 23*R*)-2,3,22,23-tetrahydroxy-5 α -ergostan-7-one tetraacetate (100 mg) in dichloromethane (2.5 mL) at 0°. The mixture was stirred at room temperature for 1 hour and then was poured into 2% potassium carbonate solution and extracted with dichloromethane. The extract was washed with water, dried, and concentrated under reduced pressure. The residue was chromatographed on silica gel. Elution with 50% hexane–ethyl acetate afforded 98 mg (96%) of product as a glass: ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.26 (m, 3 β -*H*; $W_{1/2}$ = 8 Hz), 5.22 (dd, *J* = 10.5 and 8.4 Hz, 23-*H*), 5.04 (dd, *J* = 7 and 5.4 Hz, 22-*H*), 4.86 (m, $W_{1/2}$ = 12 Hz, 2 β -*H*), 4.18 (dd, *J* = 10.5 and 8.4 Hz, 8 β -*H*), 2.72 (dd, *J* = 10 and 15 Hz, 6 β -*H*), 2.08 (s, CH_3CO), 2.05 (s, CH_3CO), 2.03 (s, CH_3CO), 1.98 (s, CH_3CO), 1.08 (s, 19-CH_3), 0.66 (s, 18-CH_3).

5.1.1.2. (endo, endo)-2,5-Dimethyl-3,9-dioxabicyclo[4.2.1]nonan-4-one (90% Trifluoroperacetic Acid Oxidation of Bridged-Ring Ketone) (447)

Trifluoroperacetic acid, prepared by dropwise addition of trifluoroacetic anhydride (7.1 mL, 50 mmol) to a stirred, ice-cold solution of 90% hydrogen peroxide (0.96 mL, 40 mmol) in 10 mL of dichloromethane (dried over magnesium sulfate and distilled), was added dropwise to a stirred, ice-cold mixture of finely ground disodium hydrogen phosphate (17.0 g, 120 mmol) in 25 mL of dichloromethane containing (*endo, endo*)-*cis*-2,4,-dimethyl-3-keto-8-oxabicyclo[3.2.1]octane (2.95 g, 20 mmol). After the reaction mixture had become too viscous for effective stirring (at approximately half addition of the peracid), the cooling bath was removed and the exothermic reaction was continued. The mixture was stirred for 2 hours at room temperature and then brought slowly to reflux for 15 minutes. The cooled mixture was filtered and the solids were washed thoroughly with dichloromethane. The combined filtrates were washed with water, 3% aqueous sodium bicarbonate, and brine, dried over magnesium sulfate, and concentrated to give an oil which crystallized on standing. Recrystallization from petroleum ether (bp 30–60°) afforded 3.2 g (94%) of product as colorless needles, mp 57–59°; IR (CCl_4) 1740 and 1180 cm^{-1}; ^{1}H NMR (CCl_4) δ 1.07 (d, *J* = 7 Hz, 3H), 1.23 (d, J = 7 Hz, 3H), 1.90 (m, 4H), 2.93 (q, *J* = 7 Hz, 1H), 4.08 (m, 2H), 4.64 (q, *J* = 7 Hz, 1H).

5.1.1.3. cis-3-Hydroxymethylcyclopentaneacetic Acid Lactone (Oxidation with 85% m-Chloroperbenzoic Acid) (445)

A mixture of bicyclo[3.2.1]octan-3-one (15 g, 0.121 mol), purified *m*-chloroperbenzoic acid (35 g, 0.49 mol), (743) and sodium bicarbonate (21 g, 0.25 mol) in 500 mL of chloroform (freed of ethanol by passing over basic alumina) was mechanically stirred in a sealed flask and in the dark for 1 week. During that time, the built-up pressure was periodically released. The mixture was filtered and the solids were washed well with chloroform. The combined filtrates were washed several times with small volumes of cold 10% sodium sulfite solution until it gave a negative test with starch–iodide paper (about 350 mL of the sulfite solution is required), then with cold sodium bicarbonate solution and dried over sodium sulfate. After the solvent was removed the remaining oil was chromatographed on a silica gel column (250 g) developed with a mixture of petroleum ether (bp 30–60°)–chloroform (4:1). Two components identified (IR and NMR) as *m*-chlorobenzoic acid [recrystallized from ether–petroleum ether (bp 30–60°), mp 156–157°] and starting material (purified by sublimation) were eluted first. The composition of the eluent was then changed to 1:1, and fractions containing the product lactone were pooled and concentrated, leaving an oil that on drying in vacuo became a waxy solid. Recrystallization from petroleum ether (bp 30–60°), including treatment with Norit, gave a total of 10.4 g (61%) of product, mp 125–129°; IR (KBr) 2980, 1725, 1460, 1420, 1390, 1340, 1320, 1260, 1215, 1160, 1090, 1040, 990, 970, 935, 875, 852, 780, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.19 (d, *J* = 3 Hz, CH_2O), 3.1–2.2 (envelope), 2.2–1.4 (envelope).

5.1.1.4. 7 β ,8 β ,-Dihydroxy-O-isopropylidene-N-carbomethoxy-3-oxa-9-azabicyclo-[4.2.1^{1,6}] nonan-4-one (A Difficult Oxidation under Forcing Conditions Using 85% m-Chloroperbenzoic Acid and a Radical Scavenger) (446)

To a solution of 6 β ,7 β -dihydroxy-*O*-isopropylidene-*N*-carbomethoxytropan-3-one (2.52 g, 9.9 mmol) in 60 mL of 1,2-dichloroethane was added 85% *m*-chloroperbenzoic acid (5.0 g, 29 mmol) and 2,4,6-tri(*tert*-butyl)phenol (20 mg). This mixture was heated to 55° and followed by gas chromatography [Hewlett Packard 700 Laboratory Chromatograph, SE-30 Ultraphase (10% w/w) with Chromosorb W support in 6 feet × 1/8 inch column]. After 22 hours the starting material had disappeared and the solution was cooled to –15° for 30 minutes to precipitate out most of the *m*-chloroperbenzoic acid. The acid was removed by filtration, and the filtrate was washed successively with cold 10% sodium bisulfite (15 mL), cold 10% sodium bicarbonate (3 × 15 mL), and saturated salt solution (20 mL). The organic phase was dried over magnesium sulfate and evaporated off, leaving a partially solidified oil. This was dissolved in anhydrous ether and allowed to crystallize at –15°, mp 117–118°. More product was obtained by adding petroleum ether (30–60°) and cooling to give a total yield 1.6 g (60%) of product; IR (CCl_4) 3000, 2960, 1755 (lactone), 1725 (urethane), 1455, 1392, and 1382 (*gem*-dimethyl) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 3H), 1.40 (s, 3H), 2.93 (m, 2H), 3.73, (s, 3H), 4.33 (bm, 4H), 4.53 (d, 1H), 4.86 (d, 1H); mass spectrum, m/z 271 (M^+), 256 (M^+ - CH_3), 240 (M^+ - OCH_3), 214, 179, 142.

5.1.1.5. Phenyl Acetate (Acid-Catalyzed Oxidation with m-Chloroperbenzoic Acid) (742)

To a solution of acetophenone (120 mg, 1 mmol) in anhydrous dichloromethane (2 mL) was added in one portion technical (80–85%) *m*-chloroperbenzoic acid (449 mg, 2.6 mmol). The suspension was cooled to 0° and distilled trifluoroacetic acid (114 mg, 1 mmol) was added dropwise over 5 minutes. The reaction flask was protected from light and the mixture was allowed to warm to room temperature; the progress of the reaction was followed by silica gel TLC. After 8 hours the mixture was diluted with dichloromethane (2 mL) and washed once each with 10% aqueous sodium sulfite solution (2 mL), saturated aqueous potassium carbonate solution (2 mL), and water (2 mL); dried over magnesium sulfate; and concentrated in vacuo to give 102 mg of pure phenyl acetate (75%).

5.1.1.6. Benzyl Benzoate (Solid-State Oxidation with m-Chloroperbenzoic Acid) (740)

A mixture of powdered benzyl phenyl ketone and 2 mol equivalents of powdered 85% *m*-chloroperbenzoic acid was ground with agate pestle and mortar. After 24 hours the excess of peroxy acid was decomposed with aqueous 20% sodium bisulfite and the product was taken up in ether. The solution was washed with aqueous 20% sodium bicarbonate and water, dried over sodium sulfate and evaporated. The crude product was chromatographed on silica gel (benzene–chloroform) to provide benzyl benzoate (97%). For comparison, the oxidation of benzyl phenyl ketone (1 g) with *m*-chloroperbenzoic acid in chloroform (50 mL) after 24 hours afforded benzyl benzoate (46%).

5.1.1.7. Isobutyl Acetate (Preparation and Use of 90% Permaleic Acid to Oxidize a Straight-Chain Ketone) (44)

To an ice-cold stirred solution of 11.6 g (0.34 mol) of 90% hydrogen peroxide and 150 mL of methylene chloride was added in one batch 39.2 g (0.4 mol) of freshly crushed maleic anhydride. When the major portion of the maleic anhydride had reacted, the solution was heated to reflux and 20 g (0.2 mol) of methyl isobutyl ketone was added in an equal volume of methylene chloride. When the theoretical amount of peracid had disappeared, as determined by iodimetric titration of aliquots, the solution was cooled, and the maleic acid was removed by filtration. The filtrate was washed twice with 100 mL of 10% sodium carbonate solution, once with 100 mL of 10% sodium bisulfite solution, and once with 100 mL of a saturated sodium chloride solution, and dried over magnesium sulfate. Distillation through a short Vigreux column yielded after removal of solvent 16.7 g (72%) of isobutyl acetate, bp 115–116°, n_D^{25} 1.3908.

5.1.1.8. 12-Hydroxydodecanoic Acid Lactone (Oxidation with 30% Permaleic Acid) (744)

Dichloromethane (1.6 L) and acetic anhydride (1.25 L) were stirred in a 5-L flask fitted with a double-surface reflux condenser and an overhead stirrer and cooled externally (ice water) while 30% hydrogen peroxide (1 L) was added. After 1 hour maleic anhydride (1 kg) was added, the mixture was cooled and stirred for 1 hour, and then the cooling bath was removed, whereupon the temperature rose during 1.5 hours and the mixture began to reflux. External cooling was resumed when needed to moderate the reaction. When little more heat was evolved, cyclododecanone (250 g, 0.62 mol) was added; this did not greatly increase the rate of heating, and when spontaneous refluxing ceased a heating mantle was used to maintain the mixture at reflux for 15 hours. The mixture was then cooled and the separated maleic acid was filtered off. The filtrate was washed in turn with water (3 × 600 mL), an aqueous solution containing 10% each of potassium hydroxide and sodium sulfite (2 × 300 mL), and then water (600 mL); tests for peroxide were now negative. After being dried (sodium sulfate) the filtrate was evaporated to give the lactone (210.4 g, 77%).

5.1.1.9. 6-endo-Benzyloxy-8-anti-methoxy-2-oxabicyclo[3.2.1]octan-3-one and 6-endo-Benzyloxy-8-anti-methoxy-3-oxabicyclo[3.2.1]octan-2-one (Oxidation with 90% Perphthalic Acid) (749)

Phthalic anhydride (0.96 g, 6.5 m mol) was dissolved in dimethylformamide (1 mL) and methylene chloride (1 mL). Hydrogen peroxide (90% in water; 0.17 g) was added to the stirred solution at 40°. After 1 hour, 6-*endo*-benzyloxy-7-*anti*-methoxybicyclo[2.2.1]heptan-2-one (0.5 g, 2 mmol) in chloroform (10 mL) was added. After stirring for 9 hours at 40° the solution was filtered and the filtrate was washed with saturated sodium sulfite solution (10 mL), saturated sodium bicarbonate solution (10 mL), and water (4 × 5 mL). The aqueous washings were back-extracted with methylene chloride (2 × 10 mL) and the combined organic extracts were dried and evaporated to give 0.44 g (83%) of a 73:27 mixture of product lactones as an oil, bp 155° (0.001 mm); IR 1740, 952, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$) of the bridgehead migrated 2-oxa-3-oxo-lactone δ 7.29 (s, C_6H_5), 4.50 (m, H-1), 4.44 (s, OCH_2Ph), 4.28 (m, H-6), 3.87 (br s, H-8), 3.28 (s, OCH_3), 3.50–2.25 (m, H-4-*exo*, H-4-*endo*, H-7-*exo*), 1.92 (dm, J = 15 Hz, H-7-*endo*); ^{13}C NMR ($CHCl_3$) δ 169.44 (s, C-3), 83.40 (d, C-8), 78.59 (d, C-1), 78.43 (d, C-6), 38.48 (d, C-5), 37.00 (t, C-4) 31.23 (t, C-7). The minor methylene migrated 3-oxa-2-oxo-lactone was identified by spectral data; ^{13}C NMR ($CHCl_3$) δ 173.33 (s, C-2), 81.19 (d, C-8), 76.90 (d, C-6), 66.40 (t, C-4), 45.14 (d, C-1), 41.59 (d, C-5), 33.33 (t, C-7).

5.1.1.10. Caprolactone (Oxidation with Magnesium Monoperphthalate) (748)

Cyclohexanone (314 mg, 3.2 mmol) was added to a stirred solution of magnesium monoperphthalate (1.39 g, 3.6 mmol) in dimethylformamide

(15 mL) at 20°. After 16 hours, the mixture was diluted with methylene chloride (50 mL) and aqueous 2 M hydrochloric acid (20 mL) was added. The organic phase was washed with a saturated aqueous solution of sodium bicarbonate and dried over magnesium sulfate. Evaporation of the solvent, after confirming the absence of peroxide, gave the lactone (208 mg, 57%).

5.1.1.11. Methyl 7-Hydroxyheptanoate (Oxidation with Persulfuric Acid) (41)
To a stirred mixture of concentrated sulfuric acid (245 mL) and water (98 mL), potassium persulfate (182 g) was added at 10°. With the temperature kept below 5°, methanol (365 mL) and then methyl 8-oxo-nonanoate (100 g, 0.537 mol) was added. After stirring at 5° for 3 hours, the mixture was poured into saturated ammonium sulfate solution (1000 mL) and extracted with ethyl acetate (3 × 500 mL). The organic layers were collected, washed with saturated sodium thiosulfate (200 mL), 5% sodium bicarbonate (2 × 50 mL), and brine (2 × 50 mL), dried with sodium sulfate, and evaporated. Product (80 g, 93%) was obtained as an oily residue, pure according to TLC (silica gel; 6:4 hexane/ethyl acetate), bp 121–123° (1.5 mm); IR (neat) 3450 (broad), 1740 (C = O), 1430 cm^{-1}.

5.1.1.12. 2-Oxo-2,5-dihydrofuran [2(5H)-furanone] (Oxidation of an Aryl Aldehyde with 30% Performic Acid) (616)
A 1-L two-necked flask, equipped with an effective reflux condenser and a dropping funnel, was charged with furfural (practical grade; 96 g, 1 mol), dichloromethane (500 mL), formic acid (92.1 g, 2 mol), sodium sulfate (100 g), and potassium carbonate (35 g). This mixture was vigorously stirred and 30% hydrogen peroxide (75 mL) was added in one portion (exothermic reaction). Vigorous stirring was continued for 30–45 minutes after which time the mixture refluxed gently. Then, 30% hydrogen peroxide (125 mL) was added dropwise with continued stirring over a 3-hour period. The mixture was allowed to cool to room temperature (10 hours) with still continued stirring. The phases, which separated at once when stirring was stopped, were isolated and the inorganic phase was extracted with dichloromethane (1 × 100 mL). The organic phases were combined and the solvent was removed on a rotary evaporator. Then toluene (200 mL) was added and formic acid was removed by azeotropic distillation. To the residue, toluene (200 mL) was added, followed by the addition of triethylamine (1–2 g), and the flask was allowed to stand for 1 hour. Toluene was evaporated and the residual liquid was distilled in vacuo over a 30-cm Vigreux column to give, after a small forerun of furfural, 43–45 g of 99% pure (GLC) product (50–54%), bp 95–96° (19 mm), 79–81° (9 mm); ^{1}H NMR ($CDCl_3$) δ 4.91 (dd, *J* = 2.2 Hz, 1.7 Hz, 2H), 6.18 (dt, *J* = 2.2 Hz, 5.8 Hz, 1H), 7.58 (dt, *J* = 1.7 Hz, 5.8 Hz, 1H).

5.1.1.13. 2′-Hydroxybiphenyl-2-carboxylic Acid Lactone (Oxidation with 90% Hydrogen Peroxide/Acetic Anhydride) (751)

To a solution of 135 g of concentrated sulfuric acid and 350 g of acetic anhydride there was slowly added with stirring and cooling 55 mL of 90% hydrogen peroxide. The temperature was maintained below 15°. To this mixture a solution of 100 g (0.56 mol) of 9-fluorenone in 100 mL of methylene chloride was added and stirring was continued for 24 hours at –5°. Addition of 500 mL of water and subsequent boiling for 1–2 hours destroyed excess acetic anhydride and peroxides and removed the methylene chloride. The solid which precipitated on cooling was collected and dissolved in the combined ethereal extracts (3 × 100 mL) from the supernatant aqueous phase. The ethereal solution was washed with 5% sodium carbonate, then brine, and finally dried over sodium sulfate. Evaporation of the solvent (steam bath or flash evaporator) yielded 96 g (89%) of crude lactone, mp 87–89.5°. Two recrystallizations from ethanol (with Norit) afforded 86.2 g (80%) of fine white crystalline needles, mp 93–94°.

5.1.1.14. 6-endo-Benzyloxy-8-anti-methoxy-2-oxabicyclo[3.2.1]octan-3-one (Oxidation with 30% Hydrogen Peroxide/Acetic Acid) (349)

To a solution of 5-*endo*-benzyloxy-7-*anti*-methoxybicyclo[2.2.1]octan-2-one (24.6 g, 0.1 mol) in 90% aqueous acetic acid (100 mL) containing sodium acetate (8.2 g, 0.1 mol) there was added 30% hydrogen peroxide (110 mL, 1 mol). After stirring for 30 hours at 50°, sodium sulfite (252 g, 2 mol) was added followed by water (200 mL). The aqueous solution was extracted with chloroform (4 × 100 mL) and the chloroform extracts were washed with water (3 × 100 mL) and saturated sodium bicarbonate solution (150 mL). The aqueous extracts were back-extracted with chloroform (2 × 100 mL) and the combined organic fractions were dried over magnesium sulfate and evaporated to give 18.3 g (70%) of product as an oil, bp 155° (0.001 mm); IR 1740, 952, 930 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.29 (s, C_6H_5), 4.50 (m, H-1), 4.44 (s, OCH_2Ph), 4.28 (m, H-6), 3.87 (br s, H-8), 3.28 (s, OCH_3), 3.50–2.25 (m, H-4-*exo*, H-4-*endo*, H-7-*exo*), 1.92 (dm, J = 15 Hz, H-7-*endo*); ^{13}C NMR ($CHCl_3$) δ 169.44 (s, C-3), 83.40 (d, C-8), 78.59 (d, C-1), 78.43 (d, C-6), 38.48 (d, C-5), 37.00 (t, C-4), 31.23 (t, C-7).

5.1.1.15. 6-(Benzyloxycarbonyl)-2-oxa-3-oxo-6-azabicyclo[3.2.2]nonane (Regioselective Oxidation with Commercial Peracetic Acid) (424)

To *N*-benzyloxycarbonyl-2-azabicyclo[2.2.2]octan-5-one (400 mg, 1.53 mmol) in 1.5 mL of acetic acid containing 0.15 g of sodium acetate was added 1.5 mL of 28% peracetic acid. After the mixture was stirred in the dark for 18 hours, 15 mL of methylene chloride was added, the solution was washed with saturated aqueous sodium sulfite (4 × 5 mL) followed by saturated aqueous sodium bicarbonate (2 × 5 mL) and dried over magnesium sulfate. Removal of solvent in vacuo afforded 338 mg (80%) of lactone; bp 145–150° (0.025 torr); ^1H NMR ($CDCl_3$) δ 7.3 (s, 5H), 5.15 (s, 2H), 4.58 (br, H-1), 4.48 (br, H-5), 4.00 (dt, J = 13, 2 Hz, H-7n), 3.55 (dd, J = 13, 4 Hz, H-7x), 3.15 (dt, J = 17, 2 Hz, H-4), 2.3–1.8 (br, 4H).

5.1.1.16. (1S,2R*)-exo-3-Phenylselenyl-cis-bicyclo[3.3.0]oct-7-ene-2-spiro-4′-γ -butyrolactone (Regioselective and Chemoselective Cyclobutanone Oxidation with Basic Hydrogen Peroxide) (195)*

A cooled (0°) basic hydrogen peroxide solution (30% aqueous hydrogen peroxide, 10.6 mL, 100 mmol; 10% aqueous sodium hydroxide, 15.1 mL) was added to 3.17 g (10.0 mmol) of (1*S**,2*R**)-*exo*-3-phenylselenyl-*cis*-bicyclo[3.3.0]oct-7-ene-2-spiro(2′-oxocyclobutane) in 70 mL of tetrahydrofuran and 35 mL of methanol at 0°. After 30 minutes, the reaction was quenched with reduction of the selenoxide by addition of an aqueous solution of sodium sulfite (35 g in 100 mL of water) and stirring for 5 minutes. The mixture was poured into a rapidly stirring mixture of 50 mL of dichloromethane and 100 mL of saturated aqueous sodium hydrogen sulfate. After 30 minutes, the organic phase was separated and the aqueous layer was extracted with 100 mL of dichloromethane followed by 2 × 100 mL of ethyl acetate. The combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuo to give an orange oil which was dissolved in about 20 mL of benzene containing a small amount of *p*-toluene-sulfonic acid. The subsequent removal of the solvent in vacuo effected a dehydration to give the lactone. Purification by flash chromatography (500 mL hexanes; 1 L ether/hexanes, 1:3, 1 L ether/hexanes, 1:2, 100 mL fractions) gave 2.3 g (70%) of a white crystalline solid, mp 110–114°, R_f 0.58 (ether); IR ($CHCl_3$) 3080, 3060, 3010, 2960, 2920, 2860, 1770, 1580, 1475, 1450, 1435, 1280, 1230, 1200, 1160, 1060, 1040, 1020, 990, 960, 950, 925 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.26 (m, 3H), 5.84 (m, 1H), 5.50 (m, 1H), 3.30 (m, 1H), 3.23 (dd, *J* = 12.5 Hz, 1H), 3.0–1.85 (m, 8H); ^{13}C NMR (15 MHz, $CDCl_3$) δ 175.4, 134.4, 132.9, 128.7, 128.5, 127.0, 126.8, 94.9, 60.0, 51.0, 41.7, 41.1, 36.9, 29.1, 26.5.

5.1.1.17. Pyrogallol 1-Monomethyl Ether (Dakin Oxidation of a Phenolic Aldehyde Using Basic Hydrogen Peroxide) (549)

The apparatus consisted of a 1-L three-necked flask fitted with a gas inlet tube extending about 3 cm into the flask and connected to the flask through a bubbler, a thermometer extending to the bottom, a mechanical stirrer, and a reflux condenser connected at the upper end with an exit tube leading to the hood. The reaction was carried out in an atmosphere of nitrogen or illuminating gas at the rate of 3 bubbles per second. In the flask were placed 60.8 g (0.4 mol) of 2-hydroxy-3-methoxybenzaldehyde and 200 mL of 2 N sodium hydroxide (0.4 mol). The mixture was stirred until almost all the solid had dissolved. The stirrer was replaced by a dropping funnel which contained 284 mL (0.5 mol) of 6% hydrogen peroxide (prepared by diluting 63 g of a solution containing 27% hydrogen peroxide with water to 284 mL). With occasional shaking, the hydrogen peroxide was added in portions of 20–25 mL. About 1 hour was required for the addition; the temperature was kept between 40 and 50°. After the addition of the first portion of hydrogen peroxide, the temperature rose to about 45° and a dark solution resulted. The temperature was allowed to fall to 40° before the next portion of the peroxide was added. After all the hydrogen peroxide was added, the reaction mixture was allowed to cool to room temperature and was then saturated with sodium chloride, after which it was extracted four times with 100-mL portions of ether. The combined extracts were dried over sodium sulfate. The ether was removed by distillation on a steam bath, and the residue was then distilled under reduced pressure. Pyrogallol monomethyl ether was collected at 136–138° (22 mm). The yield was 38–44.5 g (68–80%) of a colorless to light-yellow oil which solidified on standing.

5.1.1.18. 4-Oxahomoadamantan-5-one (Nafion-H Acid Catalysis of 30% Hydrogen Peroxide Oxidation) (323)

A mixture of adamantone (750 mg, 5 mmol) and the perfluorinated resinsulfonic acid Nafion-H (DuPont Company registered trademark, 250 mg) in dichloromethane (15 mL) was mixed with commercial 30% hydrogen peroxide (7.5 mL, 66 mmol) and stirred under reflux for 12 hours. The reaction mixture was filtered and the filtrate was extracted with dichloromethane followed by washing once with aqueous sodium bicarbonate and brine. Evaporation of solvent and direct sublimation gave glistening white crystals (798 mg, 96%) of product, mp 286–288°.

5.1.1.19. [3a α ,5(S),7a α]-3a,4,7,7a-Tetrahydro-6-methyl-5-[1-methyl-4-(tetrahydro-2H-pyran-2-yl)oxy]butyl-2-(3H)-benzofuranone (Regioselective and Chemoselective Oxidation of a Cyclobutanone with Basic tert-Butyl Hydroperoxide) (272)*

A mixture of 66 mg (0.22 mmol) of [1 α ,3(*S**),6 α]-4-methyl-3-[1-methyl-4-[(tetrahydro-2*H*-pyran-2-yl)oxybutyl]bicyclo[4.2.0]oct-3-en-7-one, 65 μL (0.66 mmol) of *tert*-butyl hydroperoxide, and 103 μL (0.26 mmol) of 10% aqueous sodium hydroxide in 2.3 mL of tetrahydrofuran cooled to 0° was stirred for 30 minutes. The reaction mixture was taken up in 50 mL of benzene–ether (1:1) and was washed with 2 mL of water and two 2-mL portions of brine. The organic layer was dried over magnesium sulfate and the solvent was evaporated in vacuo leaving 60 mg of crude lactone. Purification with 5 g of silica gel (elution with ether–benzene, 2:3) afforded 53 mg (76%) of pure product as an oil; IR (CCl_4) 2955, 2945, 2880, 1784, 1555, 1455, 1445, 1422, 1390, 1359, 1350, 1330, 1290, 1255, 1220, 1210, 1190, 1145, 1124, 1085, 1039, 998, 990, 940, 915, 868 cm^{-1}; ^1H NMR (CCl_4) δ 4.68 (m, 1H), 4.53 (br s, 1H), 1.78 (s, 3H), 0.95 (d, J = 7 Hz, 3H).

5.1.1.20. 5,5,9-Trimethyl-10-oxatricyclo[7.3.2.0^{1,6}]tetradec-6-en-11-one (Chemoselective and Regioselective Oxidation of a Bridged Ketone Using bis(Trimethylsilyl) Peroxide) (477)

To a solution of 5,5,9-trimethyltricyclo[7.2.2.0$^{1.6}$]tridec-6-en-10-one (120.2 mg, 0.517 mmol) and bis(trimethylsilyl) peroxide (521) (440 mg, 2.59 mmol) in methylene chloride (5 mL) was added boron trifluoride etherate (0.320 mL, 2.59 mmol) at –20°. After stirring 1 hour at –20 to –10°, the reaction was quenched with 5% aqueous sodium thiosulfate. The mixture was allowed to warm to room temperature and extracted with two portions of ether. The extracts were combined, washed with saturated sodium bicarbonate solution and saturated brine, dried over magnesium sulfate, and concentrated in vacuo. Chromatography (6 g of silica gel: 10:1 hexane–ethyl acetate) of the remaining oil (142.8 mg) gave 54.9 mg (43%) of product as colorless needles, mp 106–107°; IR (CCl_4) 1720 cm^{-1}; ^1H NMR (CCl_4) δ 5.50 (dd, *J* = 5.7 Hz, 4.1 Hz, 1H), 2.98 (br d, *J* = 16.2 Hz, $W_{1/2}$ = 3 Hz, 1H), 2.49 (d, *J* = 16.2 Hz, 1H), 2.5–1.2 (m, 12H), 1.32 (s, 3H), 1.11 (s, 3H), 1.09 (s, 3H); mass spectrum (13.4 eV) m/z (rel intensity) 248 (M^+,100), 233 (3.9), 206 (83.2), 189 (43.9), 188 (58.5), 179 (26.7), 177 (80.2), 166 (46.2), 82 (10.2).

5.1.1.21. Tetraphenyl- α -pyrone [Preparation and Use of bis(Trimethylsilyl) Monoperoxysulfate, a bis(Trimethylsilyl)-Buffered Reagent with Advantages over Caro's Acid] (47)

A 100-mL, three-necked, round-bottom flask, equipped with a pressure-equalizing addition funnel, Teflon spinbar, rubber septum cap, and a three-way stopcock, was attached to a nitrogen manifold. Under a nitrogen atmosphere, a solution of 1.0 g (5.6 mmol) of bis(trimethylsilyl) peroxide in 20 mL of dry methylene chloride was syringed into the reaction vessel. After the mixture was cooled to –30° with stirring, 25 mL of a 0.2 M solution of sulfur trioxide in methylene chloride was added dropwise from the addition funnel over a period of 15 minutes, carefully maintaining the reaction mixture at –30°. The reaction progress was monitored by ^1H NMR, observing the appearance of the trimethylsilyl product signal as a singlet at δ 0.40. After completion of the reaction (about 30 minutes), this solution was added to 526 mg (1.4 mmol) of tetracyclone in 10 mL of dry methylene chloride at –30° over 45 minutes. The reaction mixture was allowed to warm to room temperature (about 30°) and kept at this temperature for 8 hours. To the mixture was added 5 mL of water, the solution was transferred to a separatory funnel, the aqueous layer was siphoned off, and the methylene chloride layer was washed with 2 × 20 mL of 5% aqueous sodium bicarbonate and dried over magnesium sulfate. Rotoevaporation of the solvent and purification of the crude product by silica gel chromatography gave 417 mg (76%) of tetraphenyl- α -pyrone, IR and ^1H NMR identical with authentic material.

5.1.1.22. Phenylacetaldehyde (Regioselective Oxidation of an α , β -Unsaturated Aldehyde with 30% Hydrogen Peroxide Catalyzed by 2-Nitrophenylbenzeneperseleninic Acid) (628)

To a vigorously stirred solution of cinnamaldehyde (13.2 g, 0.1 mol) in dichloromethane (100 mL), bis(2-nitrophenyl) diselenide (1.5 g, 3.7 mmol) and 30% hydrogen peroxide (25 mL, 0.22 mol) were added. The mixture was stirred at room temperature until all aldehyde was consumed (TLC). The solid was filtered off and washed with dichloromethane and water. The filtrate was transferred to a separatory funnel and the layers were separated. The organic layer was washed with water, 5% aqueous sodium bicarbonate, 10% aqueous sodium bisulfite, again with water, and then dried over sodium sulfate. The solvent was evaporated in vacuo, the residue was dissolved in ether (100 mL), water (100 mL) and sodium bicarbonate (10 g, 0.12 mol) were added, and the mixture was vigorously stirred at room temperature for 31 hours. The organic layer was separated, washed with water, and dried over sodium sulfate. Ether was evaporated and phenylacetaldehyde was distilled at reduced pressure, bp 92° (20 mm), yield 7.5 g (63%), 2,4-dinitrophenylhydrazone mp 121°.

5.1.1.23. Phenyl Benzoate (A General Procedure for Use of Sodium Perborate, an Inexpensive Oxidant) (114)

A mixture of 4.98 g (3 mol) of sodium perborate tetrahydrate and 1.82 g (0.01 mol) of benzophenone in 30 mL of trifluoroacetic acid was stirred for 4–8 hours. The inorganic salts were removed by filtration, and ice water (about 250 mL) was added. The crude product could be isolated following extraction with methylene chloride as described previously to afford 1.60 g (81%) of product identical with known material. (42, 734)

6. Tabular Survey

The information in the following tables is an extension of examples of the Baeyer–Villiger reaction of ketones and aldehydes with peracids reviewed previously and covers the literature from January, 1954 through December, 1989. Significant reactions reported in 1990–91 are also included. The arrangement of the tables follows that used in the previous review (2) with several exceptions. The table on oxidation of alicyclic ketones has been expanded to three tables to accommodate examples of monocyclic and spirocyclic, fused bicyclic and polycyclic, and bridged bicyclic and polycyclic substrates. The table on polycarbonyl compounds includes only 1,2-dicarbonyl compounds; otherwise the structure is treated as a monocarbonyl compound. New tables on α , β -unsaturated aldehydes, ketals and acetals, and nitrogen derivatives of ketones and aldehydes have been added. The separate table for aromatic ketones has been removed and they are now listed in the appropriate sections. The tables include examples of oxidations of carbonyl compounds under Baeyer–Villiger conditions that have led to formation of products other than esters or lactones. Because hydrogen peroxide and several metal oxidants also react with ketones to afford lactones, such reactions are often considered in the current literature to be Baeyer–Villiger reactions. The tables also include examples of such Baeyer–Villiger-like oxidations because of their utility in synthesis and similarity in mechanism.

The carbonyl compounds in the tables are arranged according to total carbon content in the molecular formula of the starting ketone. Ketals and acetals are arranged according to carbon content of the parent ketone. Within each category based on carbon content, the compounds are arranged by complexity of molecular formula according to the *Chemical Abstracts* convention. When molecular formulas are identical, structures are arranged from the simpler to the more complex and from the smaller ring sizes to the larger ones.

When multiple references are cited for an entry, the conditions quoted provide the best product yield and are given in the first reference. The conditions stated refer in most cases only to the oxidation itself. Overnight reactions are reported as “12 h.” Room temperature oxidations are reported as “25°.” Product yields are in parentheses; the yield of recovered starting material is indicated by an asterisk. A dash means that the yield of product has not been reported. Subsequent references for an entry provide the same product, but may use the same or a different oxidant or an alternative set of conditions.

The following abbreviations are used in the tables:

Ac	acetyl

Bn	benzyl
BPC	*N*-benzoylperoxycarbonic acid
BTMSP	bis(trimethylsilyl) peroxide
CAN	ceric ammonium nitrate
diglyme	diethylene glycol dimethyl ether
3,5-DNPBA	3,5-dinitroperbenzoic acid
ether	diethyl ether
HMPA	hexamethylphosphoric triamide
LDA	lithium diisopropylamide
MCPBA	*m*-chloroperbenzoic acid (chloroform is always present unless otherwise stated)
MPPA	monoperphthalic acid
Nafion	a poly(perfluorosulfonic acid) (DuPont Trademark)
PAA	peracetic acid (acetic acid is always present)
PBA	perbenzoic acid (chloroform is always present unless otherwise stated)
PMA	monopermaleic acid
pN Bn	*p*-nitrobenzyl
pN PBA	*p*-nitroperbenzoic acid
PSA	persulfuric acid (sulfuric acid is always present)
TBMP	di(5-*tert*-butyl-4-hydroxy-2-methyl) sulfide
TBDMS	*tert*-butyldimethylsilyl
TBDPS	*tert*-butyldiphenylsilyl
TECTA	*N*- β , β , β -trichloroethoxycarbonyl-1,2,4-triazole
TFPAA (%)	trifluoroperacetic acid (percent hydrogen peroxide used in its preparation)
Ts	*p*-toluenesulfonyl

Table I. Reactions of Straight-Chain Ketones

View PDF

Table II. Reactions of Monocyclic and Spirocyclic Ketones

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Table III. Reactions of Fused-Ring Ketones

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Table IV. Reactions of Bridged Bicyclic and Polycyclic Ketones

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Table V. Reactions of α , β -Unsaturated Ketones

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Table VI. Reactions of 1,2-Dicarbonyl Compounds

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Table VII. Reactions of Aldehydes

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Table VIII. Reactions of α , β -Unsaturated Aldehydes

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Table IX. Peracid Reactions with Ketals and Acetals

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Table X. Peracid Reactions with Nitrogen Derivatives of Ketones and Aldehydes

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TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES

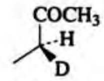
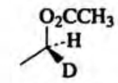
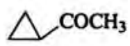
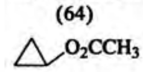
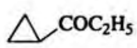
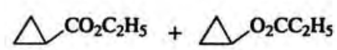
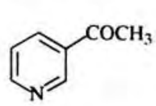
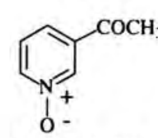
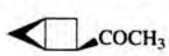
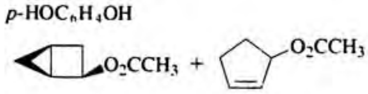
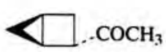
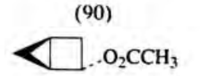
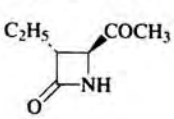
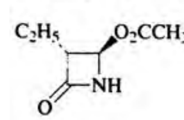
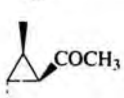
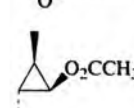
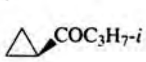
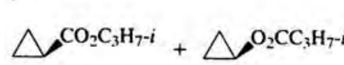
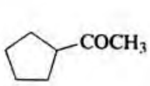
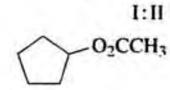
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4				
	TFPAA, Na_2HPO_4, CH_2Cl_2, 2.5 h, reflux		(12)	49
$CH_3COC_2H_5$	30% H_2O_2, polystyrene–SeO_2H, 12 h	$C_2H_5OH + CH_3CO_2H$	(90)	43
	TFPAA, Na_2HPO_4, CH_2Cl_2	$CH_3CO_2C_2H_5$	(72)	42
$CH_3COCHOHCH_3$	70% MCPBA, CH_2Cl_2, 0°	CH_3CO_2H	(—)	71
C_5				
$CH_3CD_2COCD_2CH_3$	1. TFPAA 2. KOH	$CH_3CD_2CO_2H$ (64) + CH_3CD_2OH (62)		48
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, reflux		(53)	42, 45, 734
$CH_3COC_3H_7$-*n*	TFPAA, Na_2HPO_4, CH_2Cl_2	$CH_3CO_2C_3H_7$-*n*	(78)	42
	$K_2S_2O_8$, 50% H_2SO_4	*n*-$C_3H_7OH + CH_3CO_2H$	(100)	750, 494
$CH_3COC_3H_7$-*i*	TFPAA, Na_2HPO_4, CH_2Cl_2	$CH_3CO_2C_3H_7$-*i*	(81)	42
	$K_2S_2O_8$, 50% H_2SO_4	*i*-$C_3H_7OH + CH_3CO_2H$	(100)	42
$C_2H_5COC_2H_5$	TFPAA, Na_2HPO_4, CH_2Cl_2	$C_2H_5CO_2C_2H_5$	(78)	42, 46, 532
C_6				
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, reflux	 I + II; I:II = 79:21	(≤50)	45
$CH_3COC_4H_9$-*n*	TFPAA, Na_2HPO_4, CH_2Cl_2	$CH_3CO_2C_4H_9$-*n*	(81)	42
$C_2H_5COC_3H_7$-*n*	$K_2S_2O_8$, 50% H_2SO_4	*n*-$C_3H_7OH + C_2H_5CO_2H$ +	(75)	750
		C_2H_5OH + *n*-$C_3H_7CO_2H$	(25)	
$CH_3COCH_2C_3H_7$-*i*	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, reflux	$CH_3CO_2CH_2C_3H_7$-*i*	(84)	42, 46, 765
	$K_2S_2O_8$, 50% H_2SO_4	CH_3CO_2H + *i*-$C_3H_7CH_2OH$	(100)	750
t-$C_4H_9COCH_3$	MgMPPA, CH_3OH–H_2O, 4 h, 30°	*t*-$C_4H_9O_2CCH_3$ I	(72)	748, 182
	30% H_2O_2, polystyrene–SeO_2H, 60 h	I (79) + (*t*-$C_4H_9OH + CH_3CO_2H$) II; I:II = 88:12		43, 750
$CH_3CO(CH_2)_4OH$	PAA	$HO(CH_2)_4OH$	(—)	766
C_7				
	MCPBA		(100)	100
p-$HOC_6H_4COCH_3$	3% H_2O_2, NaOH, 20 h, 28°	*p*-HOC_6H_4OH	(87)	96
	MCPBA, K_2CO_3, $CHCl_3$, 12 min, reflux	 (90) + (5) (5)*		52
	PMA, CH_2Cl_2, 1 h, warm		(90) (10)*	52
	MCPBA, C_2H_5OAc, 3 h, 50°		(72)	767
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 8 h, reflux		(67)	768
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0° 2. 3 h, 25°	 I + II; I:II = 96:4	(—)	45, 769
	MCPBA, CH_2Cl_2, 60 h, 20°		(100)	52

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

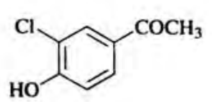
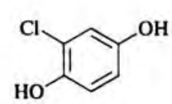
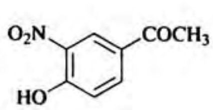
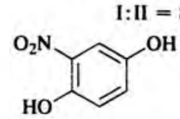
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
$CH_3COC(CH_3)_2COCH_3$	30% H_2O_2, H_2SO_4, *t*-BuOH, 1 h, 100°	*t*-$C_4H_9CO_2H$	(76) (26)*	78
$CH_3COC_5H_{11}$-*n*	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, heat	$CH_3CO_2C_5H_{11}$-*n*	(87)	42, 46, 765
$C_2H_5COC_4H_9$-*n*	*t*-BuO_2H, KOH, C_6H_5Cl, 6 h, 60°	*n*-$C_4H_9CO_2H$ major + *n*-$C_3H_7CO_2H$ + $C_2H_5CO_2H$ + CH_3CO_2H	(27)	532
	TFPAA, CH_2Cl_2	$C_2H_5O_2CC_4H_9$-*n* (I) + $C_2H_5CO_2C_4H_9$-*n* (II) I:II = 33:67	(—)	770
n-$C_3H_7COC_3H_7$-*n*	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, heat	*n*-$C_3H_7CO_2C_3H_7$-*n*	(80)	42
	$[(CH_3)_3Si]_2SO_5$, CH_2Cl_2, 8 h, 30°	"	(96)	47
n-$C_3H_7COC_3H_7$-i	H_2O_2, CH_3OH, reflux	*i*-$C_3H_7CO_2H$ (2) + *n*-$C_3H_7CO_2H$ (5)	(82)*	494
C_8				
$C_6H_5COCF_3$	TFPAA, $CHCl_3$, 5 h, 70°	$C_6H_5CO_2H$ (I) + C_6H_5OH (II) I:II = 93:7	(72)	113
p-$BrC_6H_4COCH_3$	$[(CH_3)_3Si]_2SO_5$, CH_2Cl_2, 8 h, 30°	*p*-BrC_6H_4OH	(98)	47, 114
	MCPBA, $CHCl_3$, 25°	*p*-$BrC_6H_4O_2CCH_3$	(50)	740
	MCPBA (2 eq), solid state, 5 d, 25°	"	(64)	740
p-$ClC_6H_4COCH_3$	90% H_2O_2, P_2O_5, 30°	*p*-$ClC_6H_4O_2CCH_3$	(95)	28
	TFPAA (90%), CH_2Cl_2, 20 h, 25°	*p*-ClC_6H_4OH *p*-$ClC_6H_4CO_2H$	(42) (1) (64)*	15
	t-BuO_2H, KOH, 80°	*p*-$ClC_6H_4CO_2H$	(12) (70)*	532
	3% H_2O_2, NaOH, 12 h, 35°		(47) (44)*	97
	20% PAA, AcOH, 48 h, 35° and 1 h, 68°	"	(29) (29)*	97
o-$O_2NC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*o*-$O_2NC_6H_4OH$ (I) + *o*-$O_2NC_6H_4CO_2H$ (II) I:II = 6:94	(38) (24)*	113
m-$O_2NC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*m*-$O_2NC_6H_4O_2CCH_3$ (I) + *m*-$O_2NC_6H_4CO_2CH_3$ (II) I:II = 67:33	(—)	113
p-$O_2NC_6H_4COCH_3$	TFPAA (90%), CH_2Cl_2, 2 d, 25°	*p*-$O_2NC_6H_4OH$ (I) + *p*-$O_2NC_6H_4CO_2H$ (II) I:II = 88:12	(70)	15
	3% H_2O_2, NaOH, 12 h, 35°		(2) (95)*	97
	20% PAA, AcOH, 48 h, 35°, then 1 h, 60°	"	(35) (46)*	97
$C_6H_5COCH_3$	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, heat	$C_6H_5O_2CCH_3$ I (major) $C_6H_5CO_2CH_3$ II (trace)	(90)	15, 113, 114 761, 765, 771
	MCPBA (85%), CF_3CO_2H, CH_2Cl_2, 8 h, 0–25°	I	(75)	742, 124
	t-BuO_2H, KOH, benzene, 18-crown-6, 1 h, 70°	$C_6H_5CO_2H$	(45) (55)*	122, 124, 182
p-$HOC_6H_4COCH_3$	3% H_2O_2, NaOH, 20 h, 28°	*p*-HOC_6H_4OH	(87)	96, 772

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

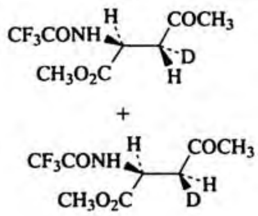
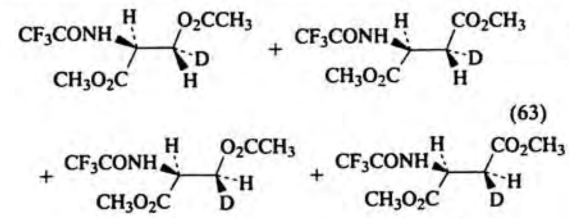
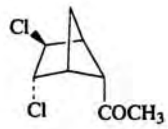
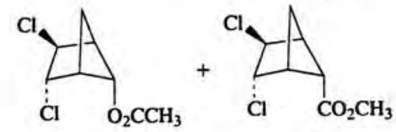
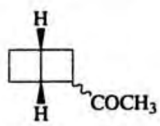
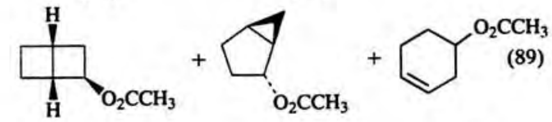
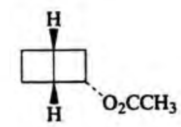
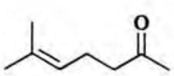
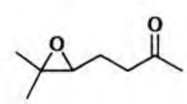
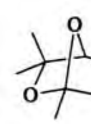
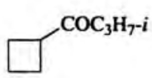
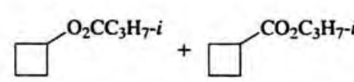
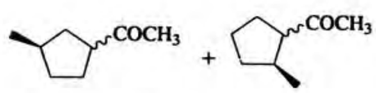
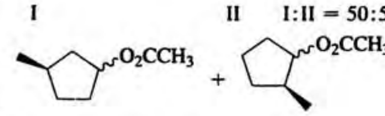
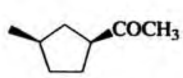
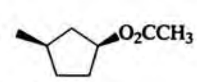
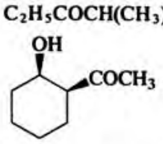
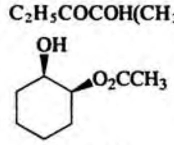
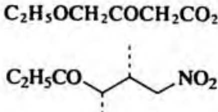
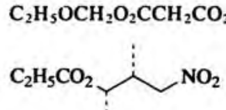
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (85%), CH_2Cl_2, 2.5 h, reflux	 (63) I:II = 75:25	89, 90, 87, 88
	1. TFPAA (90%), CH_2Cl_2, 1 h, 0° 2. 24 h, 25°	 (80) (10)	773
 endo/exo 38/62	MCPBA, CH_2Cl_2, 3 d, 25°	 I II III (89) I:II:III = 91:9:1	662
endo/exo 65/35	MPPA, ether, 2 h, 25°	 IV I:II:III:IV = 40:32:9:19 (83)	662
	40% PAA, NaOAc, CH_2Cl_2, 25°	 (90)	102, 635
	MCPBA, CH_2Cl_2, 1 h, 25°	 (80)	635
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0° 2. 3 h, 25°	 I II I:II = 50:50 (—)	769
	PNPBA, $CHCl_3$, 48 h, 25°	 (89)	680
	PNPBA, $CHCl_3$, 48 h, 25°	 (89)	680
$CH_3COC_6H_{11}$	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, reflux	$CH_3CO_2C_6H_{11}$ (53)	42
$C_2H_5COCH(CH_3)COC_2H_5$	MPPA, ether, 25°	$C_2H_5COCOH(CH_3)COC_2H_5$ (47)	76
	DNPBA, CH_2Cl_2, 17 h, 25°	 (41)	85
$CH_3COC(CH_3)_2CO_2C_2H_5$	1. 98% H_2O_2, H_2SO_4 2. benzene, 6 h, heat	t-$C_4H_9CO_2H$ (75)	774
$C_2H_5OCH_2COCH_2CO_2C_2H_5$	MCPBA, $CHCl_3$, 25°	$C_2H_5OCH_2O_2CCH_2CO_2C_2H_5$ (70–80)	79a
	MCPBA, CH_2Cl_2, 17 d, 25°	 (90)	775

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

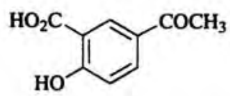
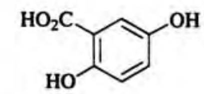
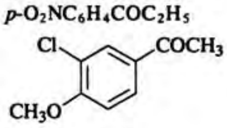
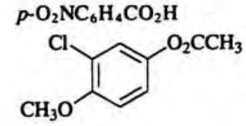
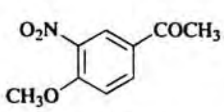
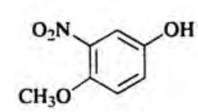
	Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_3COC_6H_{13}$-*n*	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 11 h, 25°	$CH_3CO_2C_6H_{13}$-*n* (69)	220, 221, 494, 46
	$CH_3CO(CH_2)_6OH$	96% H_2O_2, H_2SO_4	$CH_3CO_2(CH_2)_6OH$ + $HO(CH_2)_6OH$ (50) (50)	776
	n-$C_4H_9COCH_2N(CH_3)_2$	30% H_2O_2, C_2H_5OH, 1–14 d	*n*-$C_4H_9CO_2H$ + $(CH_3)_2NCHO$ (—)	73
C_9	*o*-$HO_2CC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*o*-$HO_2CC_6H_4OH$ (I) + *o*-$HO_2CC_6H_4CO_2H$ (II) (42); I:II = 94:6	113
	p-$HO_2CC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*p*-$HO_2CC_6H_4OH$ (I) + *p*-$HO_2CC_6H_4CO_2H$ (II) (86); I:II = 97:3	113
		3% H_2O_2, NaOH, 12 h, 35°	 (63) (26)*	97
		1. 20% PAA, AcOH, 48 h, 35° 2. 1 h, 60°	" (45) (40)*	97
	p-$ClC_6H_4CH_2COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 4.5 h, 55°	*p*-$ClC_6H_4CH_2OH$ (6) + *p*-ClC_6H_4CHO (1) + *p*-$ClC_6H_4CO_2H$ (89)	777
	o-$O_2NC_6H_4COC_2H_5$	TFPAA, $CHCl_3$, 5 h, 70°	*o*-$O_2NC_6H_4OH$ (I) + *o*-$O_2NC_6H_4CO_2H$ (II) (27); I:II = 2:98	113
	m-$O_2NC_6H_4COC_2H_5$	TFPAA, $CHCl_3$, 5 h, 70°	*m*-$O_2NC_6H_4CO_2H$ (90)	113
	p-$O_2NC_6H_4COC_2H_5$	TFPAA, $CHCl_3$, 5 h, 70°	*p*-$O_2NC_6H_4CO_2H$ (100)	113
		1. 20% PAA, AcOH, 48 h, 35° 2. 1 h, 60°	 (70)	97
		1. 20% PAA, AcOH, 48 h, 35° 2. 1 h, 60°	 (87) (6)*	97
	$C_6H_5CH_2COCH_3$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h	$C_6H_5CH_2O_2CCH_3$ (I) (95–97)	778, 771
		$NaBO_3$, TFAA–AcOH, 4–8 h, 25°	I (88)	114
		H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 7 h, 55°	$C_6H_5CH_2OH$ (8) + C_6H_5CHO (3) + $C_6H_5CO_2H$ (80)	777
	p-$CH_3C_6H_4COCH_3$	$NaBO_3$, TFAA–AcOH, 4–8 h, 25°	*p*-$CH_3C_6H_4O_2CCH_3$ (79)	114, 779
		t-BuO_2H, KOH, 80°	*p*-$CH_3C_6H_4CO_2H$ (3) (84)*	122
	$C_6H_5COC_2H_5$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, reflux	$C_6H_5O_2CC_2H_5$ (87) + $C_6H_5CO_2C_2H_5$ (6)	15, 124
		t-BuO_2H	$C_6H_5CO_2H$ (60) + (40)*	15, 124
	$CH_3CHOHCOC_6H_5$	70% MCPBA, CH_2Cl_2, 0°	" (40)	71
	$C_6H_5CHOHCOCH_3$	70% MCPBA, CH_2Cl_2, 0°	C_6H_5CHO (81)	71
	o-$CH_3OC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*o*-$CH_3OC_6H_4OH$ (I) + *o*-$CH_3OC_6H_4CO_2CH_3$ (II) (73–82); I:II = 87–90:13–10	113
	m-$CH_3OC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*m*-$CH_3OC_6H_4O_2CCH_3$ (I) + *m*-$CH_3OC_6H_4CO_2CH_3$ (II) (48–55); I:II = 63–76:38–24	113
	p-$CH_3OC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	*p*-$CH_3OC_6H_4O_2CCH_3$ (I) + *p*-$CH_3OC_6H_4CO_2CH_3$ (II) (75–80); I:II = 84–88:16–12	113
		$NaBO_3$, TFAA–AcOH, 4–8 h, 25°	I (81)	114, 600
	p-$HOC_6H_4COC_2H_5$	3% H_2O_2, NaOH, CH_3COCH_3, 32 h, 40°	*p*-HOC_6H_4OH (82)	96

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

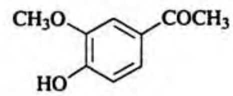
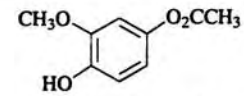
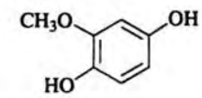
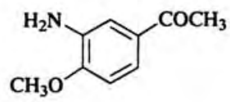
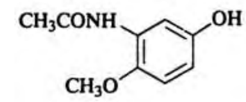
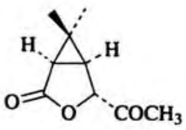
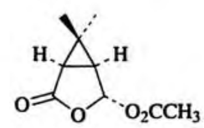
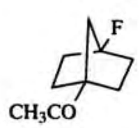
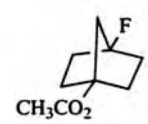
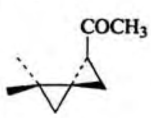
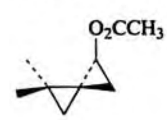
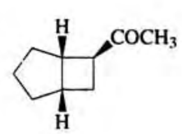
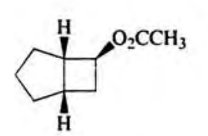
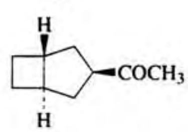
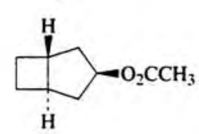
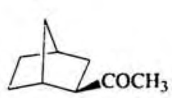
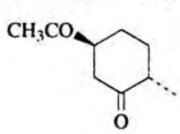
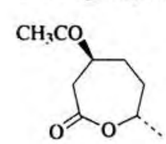
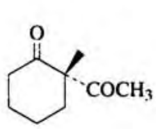
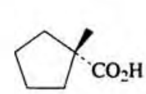
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, H_2O, pH 3, 1 h, 60°	 +	(37)	572
			(5) (27)*	
	1. 20% PAA, AcOH, 1 h, 60° 2. 48 h, 35°		(50) (36)*	97
	85% MCPBA, CH_2Cl_2, 12 h, 25°		(87)	68
	85% MCPBA, CH_2Cl_2, 14 d, 45°		(69)	780
	TFPAA		(—)	781
	PNPBA, $CHCl_3$, 48 h, 25°		(88)	679
	MCPBA, $CHCl_3$, 20 h, 25°		(91)	782
	PBA, $CHCl_3$, 163 h, 25°		(85)	13
	MCPBA, CH_2Cl_2, 25°		(79)	110
	28% H_2O_2, H_2O, 12 h, 20°		(90)	202, 78
		+ $HO_2(CH_2)_4CO_2H$	(4)	
		+ $HO_2CC(CH_3)_2(CH_2)_4CO_2H$	trace	

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

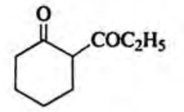
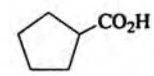
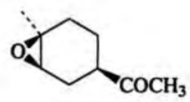
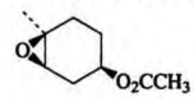
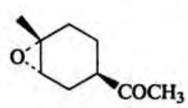
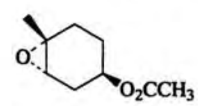
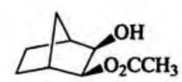
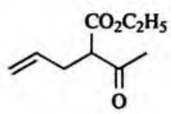
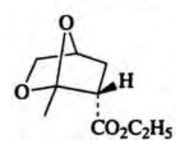
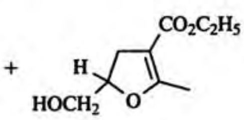
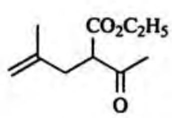
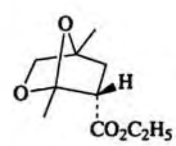
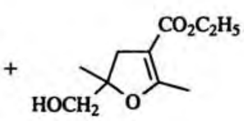
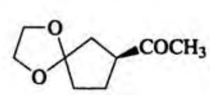
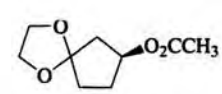
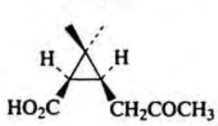
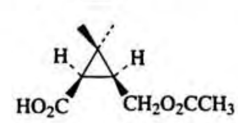
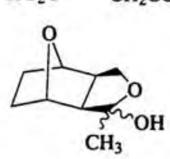
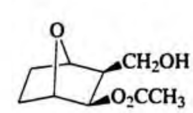
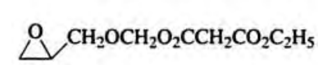
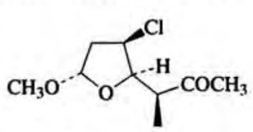
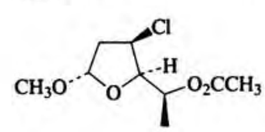
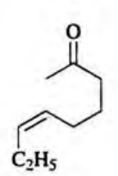
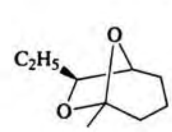
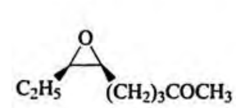
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, NaOH, 1 h, 20–25°	 +	(59)	204
		$HO_2C(CH_2)_4CO_2H$	(4)	
	MCPBA, $CHCl_3$, 12 h, 25°		(76)	783
	MCPBA, $CHCl_3$, 12 h, 25°		(76)	783
	TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 0°		(72)	85
	MCPBA, CH_2Cl_2, 12 h, 25°	 + 	(—)	635
	MCPBA, CH_2Cl_2, 12 h, 25°	 + 	(—)	635
	MCPBA, $CHCl_3$, 3 d		(—)	784
	MCPBA, CH_2Cl_2, 72 h, 25°		(69)	68
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 48 h, 25°		(>68)	58
$CH_2{=}CHCH_2OCH_2COCH_2CO_2C_2H_5$	MCPBA, $CHCl_3$, 25°		(70–80)	79a
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 5 h, 20°		(85)	382
	85% MCPBA, CH_2Cl_2, 1 h, 0°, then $HClO_4$		(79)	207
	PBA, CH_2Cl_2		(100)	785, 786, 787

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

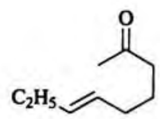
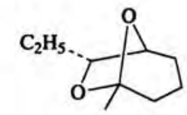
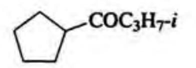
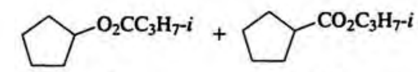
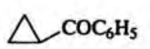
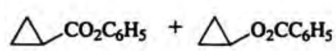
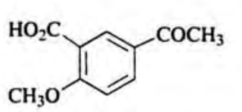
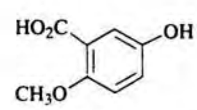
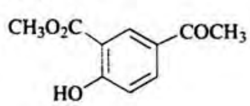
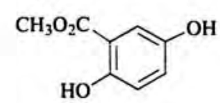
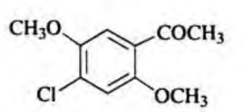
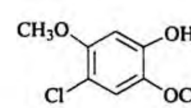
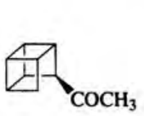
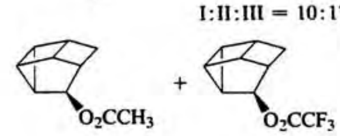
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	85% MCPBA, CH_2Cl_2, 1 h, 0°, then $HClO_4$	 (80)	207
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0° 2. 3 h, 25°	 I:II = 50:50 (—)	769
n-$C_4H_9COC_4H_9$-n	90% H_2O_2, polystyrene–AsO_3H_2, dioxane, 32 h, 80°	(0)	182
i-$C_3H_7CH_2COCH_2C_3H_7$-i	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, heat	i-$C_3H_7CH_2CO_2CH_2C_3H_7$-i (81)	42, 221
$(CH_3)_3Si(CH_2)_2COC_3H_7$-$i$	MCPBA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	$(CH_3)_3Si(CH_2)_2O_2CC_3H_7$-$i$ (I) + $(CH_3)_3Si(CH_2)_2CO_2C_3H_7$-$i$ (II) (80) I:II = 67:33	94
C_{10}			
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, reflux	 I:II = 97:3 (—)	45
o-$CH_3O_2CC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h, 70°	o-$CH_3O_2CC_6H_4CO_2CH_3$ (I) + o-$CH_3O_2CC_6H_4O_2CCH_3$ (II) (73) I:II = 12:88	113
p-$CH_3O_2CC_6H_4COCH_3$	TFPAA, $CHCl_3$, 5 h 70°	p-$CH_3O_2CC_6H_4CO_2CH_3$ (I) + p-$CH_3O_2CC_6H_4O_2CCH_3$ (II) (77) I:II = 96:4	113
	20% PAA, AcOH, 48 h, 35°, 1 h, 60°	 (53)	97
	20% PAA, AcOH, 48 h, 35°, 1 h, 60°	 (51) (36)*	97
	3% H_2O_2, NaOH	(20) (50)*	97
	PAA, NaOAc, AcOH, 12 h, 40–42°	 (44)	788
$C_6H_5COC_3H_7$-n	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat	$C_6H_5O_2CC_3H_7$-n (85) + $C_6H_5CO_2C_3H_7$-n (6)	15
	H_2O_2, CH_3OH, heat	$C_6H_5CO_2H$ (11) + $C_2H_5CO_2H$ (trace)	494
$C_6H_5COC_3H_7$-i	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, heat	$C_6H_5CO_2C_3H_7$-i (63) + $C_6H_5O_2CC_3H_7$-i (33)	15, 124
	t-BuO_2H, KOH	$C_6H_5CO_2H$ (40) (60)*	124, 532
$C_6H_5(CH_2)_2COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 10 h, 55°	$C_6H_5(CH_2)_2OH$ (I) + $C_6H_5CH_2CHO$ (II) I:II = 93:7 (42) (55)	777
$C_6H_5CH(CH_3)COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 28 h, 45°	$C_6H_5CHOHCH_3$ (I) + $C_6H_5COCH_3$ (II) I:II = 31:69 (58) (40)	777
p-$CH_3C_6H_4CH_2COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 6 h, 55°	p-$CH_3C_6H_4CH_2OH$ (I) + p-$CH_3C_6H_4CHO$ (II) + p-$CH_3C_6H_4CO_2H$ (III) (95) I:II:III = 10:17:73	777
	TFPAA, Na_2HPO_4, CH_2Cl_2, 5 h, heat	 I:II = 50:50 (90)	658

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

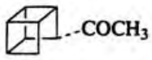
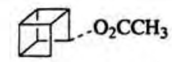
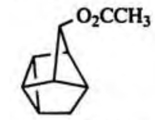
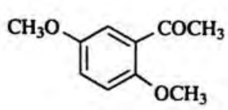
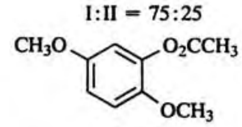
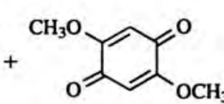
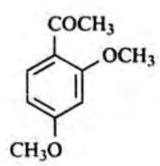
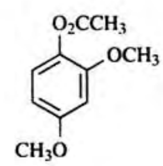
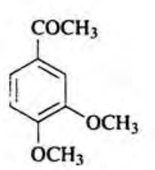
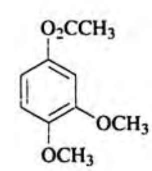
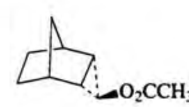
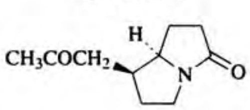
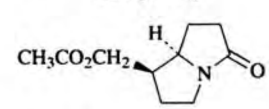
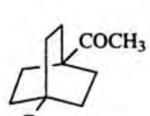
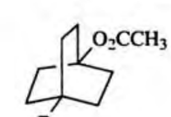
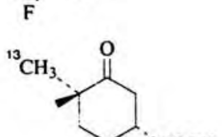
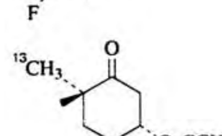
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat		(97)	658
	PBA		(>74)	789
p-$CH_3OC_6H_4CH_2COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 4 h, 55°	p-$CH_3OC_6H_4CH_2OH$ (I) + p-$CH_3OC_6H_4CHO$ (II) + p-$CH_3OC_6H_4CO_2H$ (III); I:II:III = 26:34:40	(62)	777
$CH_3COCHOHCH_2C_6H_5$	1. 30–35% H_2O_2, NaOH, CH_3OH, 5 min, 0° 2. CH_2N_2	$C_6H_5CH_2CO_2CH_3$ + $C_6H_5CO_2CH_3$ + C_6H_5CHO	(70) (20) (10)	72
$C_6H_5CHOHCH_2COCH_3$	DNPBA, TBP, $ClCH_2CH_2Cl$, 3 h, heat	$C_6H_5CHOHCH_2O_2CCH_3$ (I) + $C_6H_5CH(O_2CCH_3)CH_2OH$ (II); I:II = 75:25	(80)	85
	36–40% PAA, NaOAc, AcOH, 12 h, 40–42°	 (68–78) +  (3)		788
	90% H_2O_2, $[2,4$-$(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 81 h, 25°		(65)	628
	90% H_2O_2, $(2$-$O_2NC_6H_4Se)_2$ CH_2Cl_2, 168 h, 25°		(67)	628
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.75 h, heat		(72)	790
	TFPAA (90%), CH_2Cl_2, 3 h, 25°		(56)	65
	MCPBA, CH_2Cl_2, 3 d, 25°		(77)	791
	MCPBA, CH_2Cl_2, 64 h, 25°		(77)	107

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

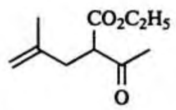
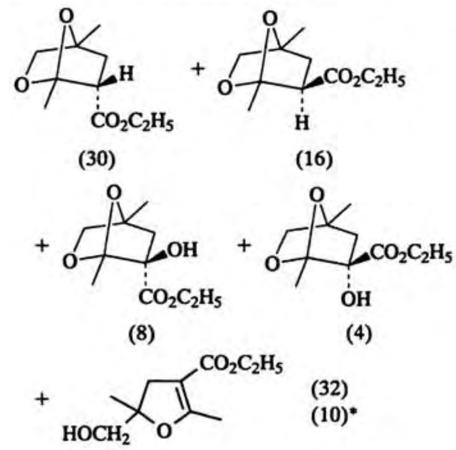
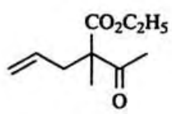
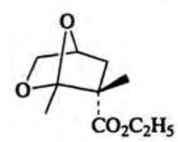
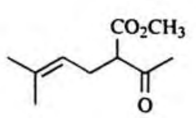
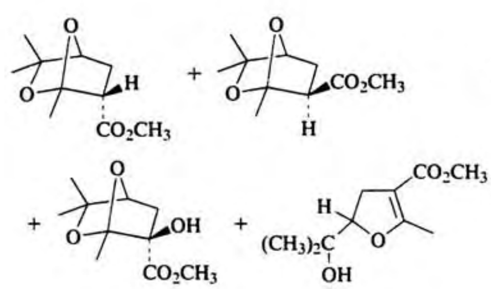
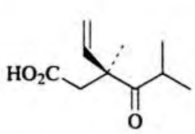
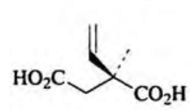
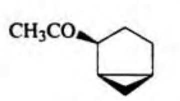
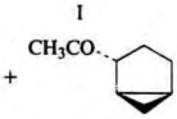
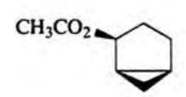
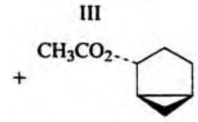
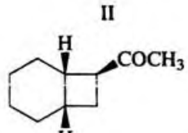
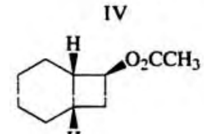
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	80% MCPBA, CH_2Cl_2, 12 h, 25°	 (30) + (16) + (8) + (4) + (32) (10)*	635
	80% MCPBA, CH_2Cl_2, 12 h, 25°	 (—)	635
	80% MCPBA, CH_2Cl_2, 12 h, 25°	 (—)	635
	30% H_2O_2, NaOH, 4 h	 (100)	106
 I +  II; I:II = 91:9	PBA, $CHCl_3$, 10 d, 25°	 III +  IV; III:IV = 91:9 (75)	792
	PNPBA, $CHCl_3$, 48 h, 25°	 (89)	679

TABLE I. Reactions of Straight-Chain Ketones (*Continued*)

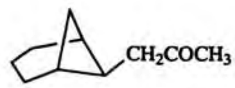
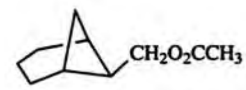
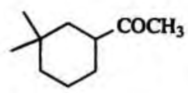
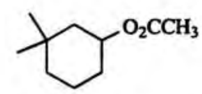
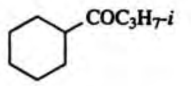
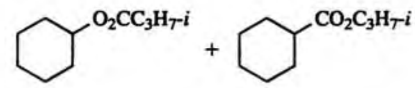
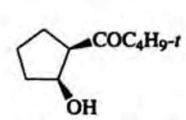
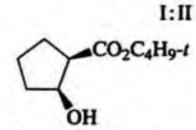
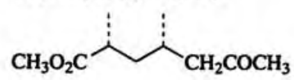
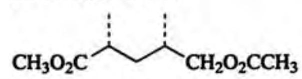
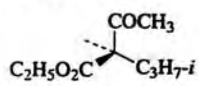
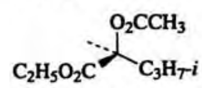
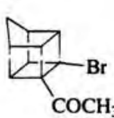
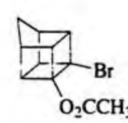
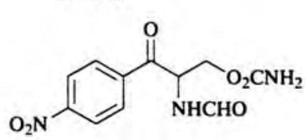
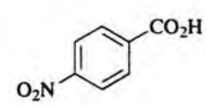
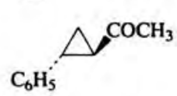
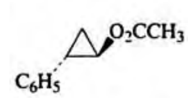
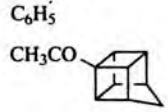
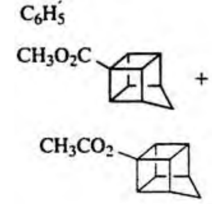
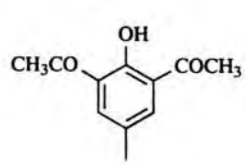
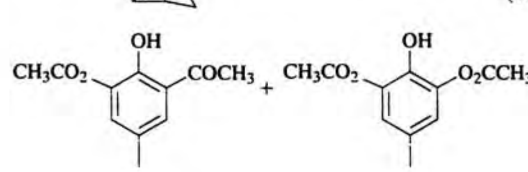
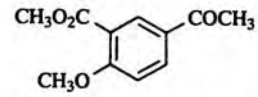
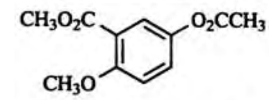
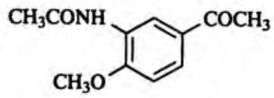
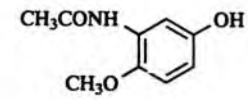
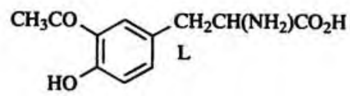
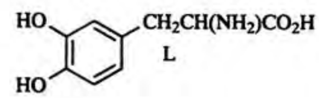
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA	 (84)	793
	36% PAA, NaOAc, $CHCl_3$, 12 h, 25°	 (—)	794
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0° 2. 3 h, 25°	 I + II (—) I:II = 60:40	769
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat	 (40)	86
$CH_3CO(CH_2)_6CO_2CH_3$	$K_2S_2O_8$, H_2SO_4, H_2O, 3 h, 5°	$HO(CH_2)_6CO_2CH_3$ (93)	41
	TFPAA, Na_2HPO_4, CH_2Cl_2	 (64)	141
 (*R*)	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 (*S*) (89)	79
n-$C_6H_{13}CHOHCH_2COCH_3$	DNPBA, Na_2HPO_4, TBP, $ClCH_2CH_2Cl$, 3 h, reflux	*n*-$C_6H_{13}CH(O_2CCH_3)CH_2OH$ I (70) + *n*-$C_6H_{13}CHOHCH_2O_2CCH_3$ II 70:30 mixture	85
$(CH_3)_3Si(CH_2)_2COC_4H_9$-*t*	MCPBA, Na_2HPO_4, TBP, CH_2Cl_2, 4 h, reflux	$(CH_3)_3Si(CH_2)_2O_2CC_4H_9$-*t* I + $(CH_3)_3Si(CH_2)_2CO_2C_4H_9$-*t* II (79) I:II = 33:67	94
C_{11}			
	TFPAA (98%), Na_2HPO_4, CH_2Cl_2, 15 h, 25°	 (59)	795
	6% PAA, H_2SO_4, 10 h, 20°	 (90)	74
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, reflux to 25°	 (77)	796
	TFPAA (85%), Na_2HPO_4, CH_2Cl_2, 1 h, heat	 (69) + (4) (21)*	797
	MCPBA (3.5 eq.), TFAA, $CHCl_3$	 (39) + trace	798

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. 20% PAA, AcOH, 48 h, 35° 2. 1 h, 60°		(60)	97
	1. 20% PAA, AcOH, 48 h, 35° 2. 1 h, 60°		(70) (10)*	97
	6% H_2O_2, NaOH, 5 h, 35–40°		(81)	96
	30% H_2O_2, NaOH, H_2O, 40 min, 44–35°	"	(75)	95
$C_6H_5CH_2CH(CH_3)COCH_3$	PBA, $CHCl_3$, 15 d, 25°	$C_6H_5CH_2CH(CH_3)O_2CCH_3$	(84)	799
$C_6H_5COC_4H_9$-*t*	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, reflux	$C_6H_5O_2CC_4H_9$-*t* + $C_6H_5CO_2C_4H_9$-*t* (77) (2)	(12)*	15, 124
	t-BuO_2H	$C_6H_5CO_2H$	(40) +(60)*	122, 124
$C_6H_5C(CH_3)_2COCH_3$	H_2O_2 (0.4 M), NaOH, C_2H_5OH–H_2O, 64 h, 45°	$C_6H_5C(CH_3)_2OH$	(13) +(83)*	777
$C_6H_5CHOHCH_2COC_2H_5$	DNPBA, TBP, $ClCH_2CH_2Cl$, 3 h, heat	$C_6H_5CHOHCH_2CO_2C_2H_5$ I + $C_6H_5CHOHCH_2O_2CC_2H_5$ II + $C_6H_5CH(O_2CC_2H_5)CH_2OH$ III I:II:III = 68:23:9	(83)	85

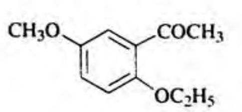
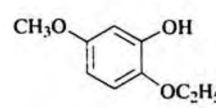
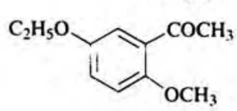
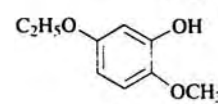
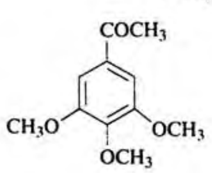
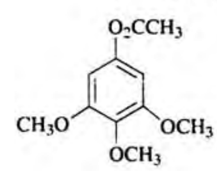
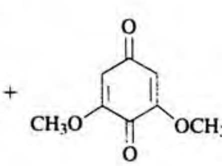
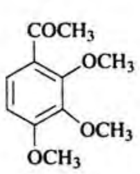
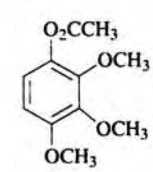
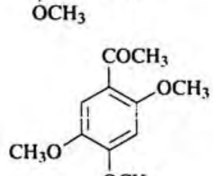
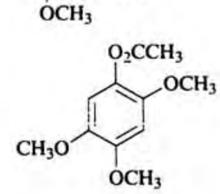
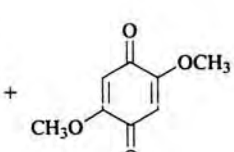
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, NaOAc, AcOH, 12 h, 40–42°		(43)	788
	PAA, NaOAc, AcOH, 12 h, 40–42°		(23)	788
	35% PAA, $HClO_4$, Ac_2O, 3 h, 5°	 +  I II I:II = 92:8	(60)	607
	30% H_2O_2, 5% $HClO_4$, TsOH, AcOH, 3 h, 25°	I:II = 83:17	(60)	675
	35% PAA, $HClO_4$, Ac_2O, 2 h, 30°		(96)	607, 628, 800
	35% PAA, $HClO_4$, Ac_2O, 3 h, 1°	 +  (85) (6)		607

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

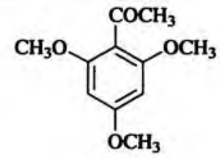
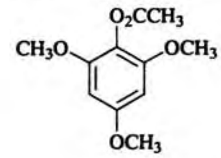
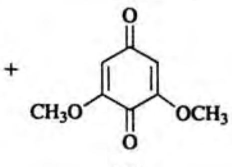
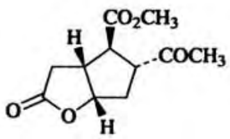
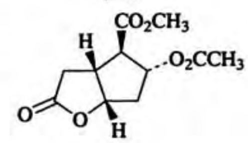
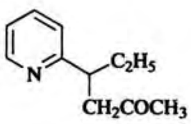
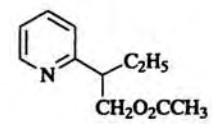
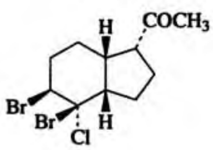
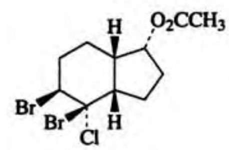
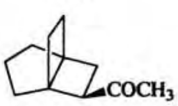
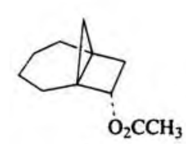
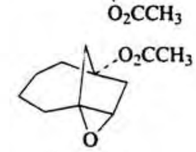
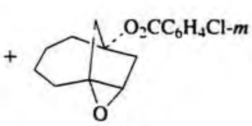
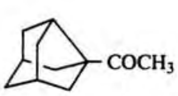
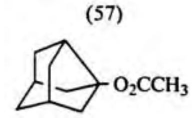
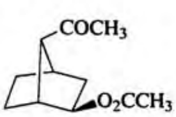
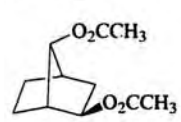
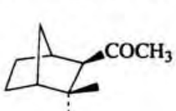
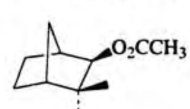
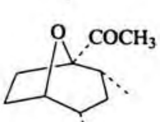
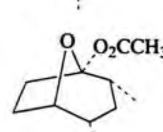
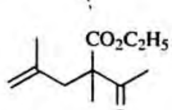
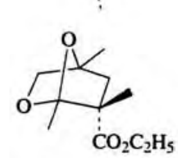
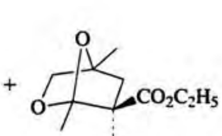
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	35% PAA, $HClO_4$, Ac_2O, 5 h, 5°	 (65) +  (10)	607
	TFPAA, Na_2HPO_4, CH_2Cl_2, 10 h, 25°	 (65)	801
	PBA, $CHCl_3$, 14 d, 25°	 (78)	98
	MCPBA, $CHCl_3$	 (—)	802, 803
	MCPBA	 (100)	804
	MCPBA, CH_2Cl_2, 25°	 (100)	657
	MCPBA, CH_2Cl_2, 25°	 (57) +  (27)	657
	no data	 (—)	805
	TFPAA	 (70)	806
	MCPBA, $CHCl_3$, 20 h, 25°	 (76)	807
	MCPBA, CH_2Cl_2, 4 d, 25°	 (>60)	75
	MCPBA, CH_2Cl_2	 +  (—)	635

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

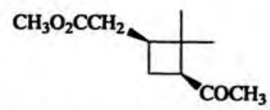
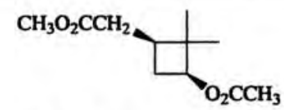
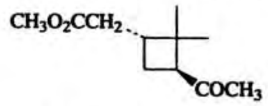
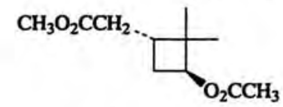
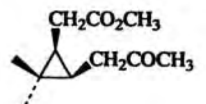
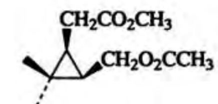
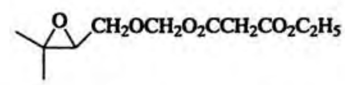
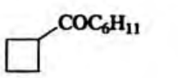
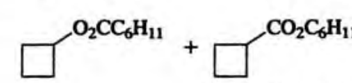
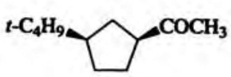
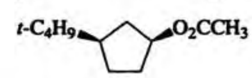
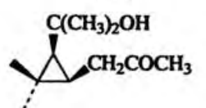
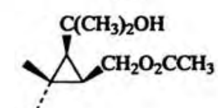
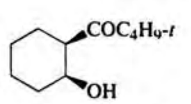
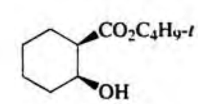
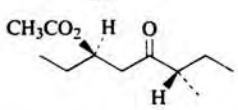
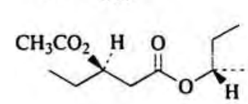
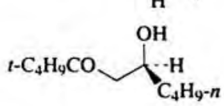
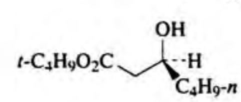
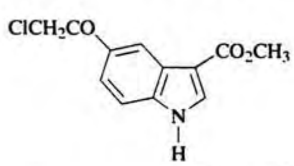
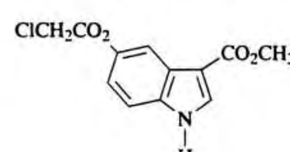
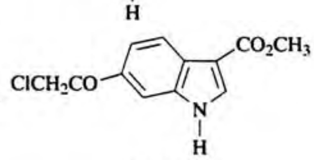
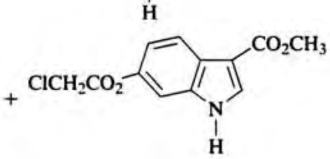
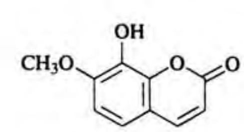
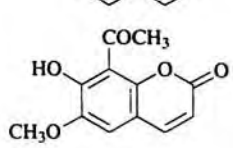
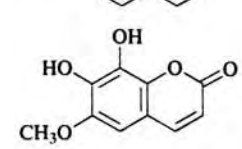
	Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
		80% MCPBA, CH_2Cl_2, 3 d, 25°		(99)	808, 809
		MCPBA, $CHCl_3$, 5 d, 25°		(92)	810
		1. PMA (90%), CH_2Cl_2, 4 h, 40–45° 2. 20 h, 25°		(93)	811, 50
	$(CH_3)_2C{=}CHCH_2OCH_2COCH_2CO_2C_2H_5$	MCPBA, $CHCl_3$, 25°		(70–80)	79a
		1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0° 2. 3 h, 25°	 I II I:II = 50:50	(—)	769
		PNPBA, $CHCl_3$, 48 h, 25°		(92)	680
		PBA, $CHCl_3$, 96 h, 25°		(75)	812
		TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat		(<10)	86
		MCPBA, $CHCl_3$, 8 d, 25°		(72)	813
		TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat		(54)	86
C_{12}		MCPBA, Na_2HPO_4, $CHCl_3$, 8 h, 20°		(56)	121
	+  mixture		+ 	(23)	
		30% H_2O_2, NaOH, 2 h, 0°		(—)	814
		H_2O_2, NaOH, 0°		(56)	815

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

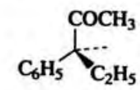
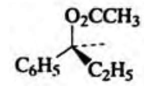
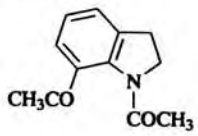
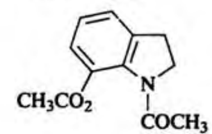
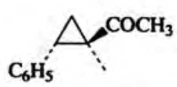
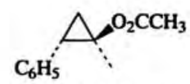
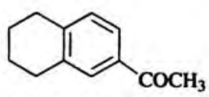
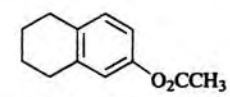
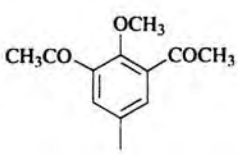
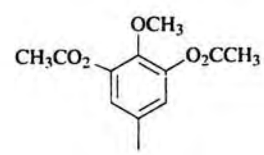
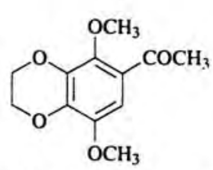
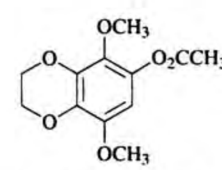
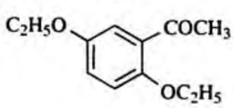
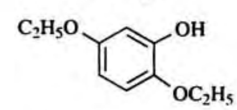
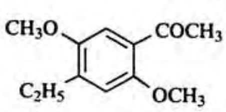
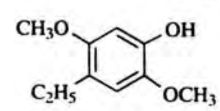
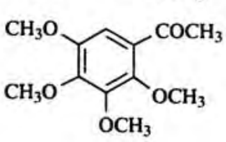
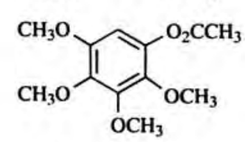
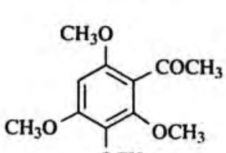
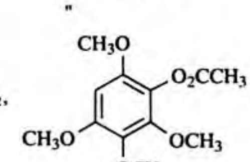
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PBA, $CHCl_3$, 14 d, 25°		(—)	816
	TFPAA, Na_2HPO_4, CH_2Cl_2		(20–25)	722
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 6 h, 10–25°		(77)	817
$C_6H_5COC_5H_{11}$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat	$C_6H_5CO_2C_5H_{11}$ (48) + $C_6H_5O_2CC_5H_{11}$ (44)		15
p-$CH_3C_6H_4COC_4H_9$-*n*	MCPBA, CF_3CO_2H, CH_2Cl_2, 8 h, 0–25°	*p*-$CH_3C_6H_4O_2CC_4H_9$-*n*	(100)	742
	MCPBA, $CHCl_3$, 24 h, reflux		(76)	764
$CH_3COCH(CH_2C_6H_5)COCH_3$	MPPA, ether, 7 d	$CH_3CO(CH_2)_2C_6H_5$ + $C_6H_5CH_2CO_2H$ + $C_6H_5CH_2COCOCH_3$ + CH_3CO_2H	(—)	76
$CH_3CO(CH_2)_2CO_2CH_2C_6H_5$	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, heat	$CH_3CO_2(CH_2)_2CO_2CH_2C_6H_5$	(63)	818
	MCPBA, TFAA–$CHCl_3$, 2 d, 25°		(60)	819
	36% H_2O_2, HCO_2H, 26 h, −5–0°		(60)	820
	PAA, NaOAc, AcOH, 12 h, 40–42°		(45)	788
	1. 30% PAA, TsOH, AcOH, 3 h, 60–65° 2. 24 h, 20°		(47)	591
	90% H_2O_2, $(2\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 48 h, 25°		(81)	628
	35% PAA, 15 min, 5–6°	"	(70)	607
	90% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 140 h, 25°		(27) (27)*	628

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

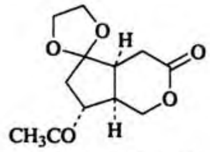
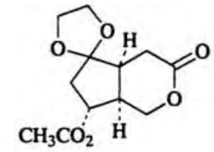
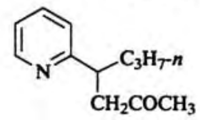
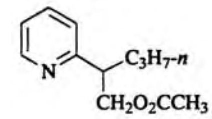
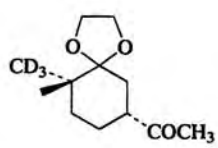
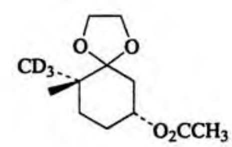
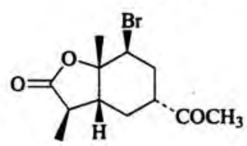
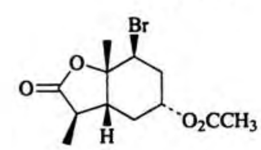
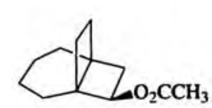
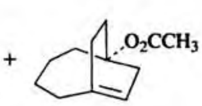
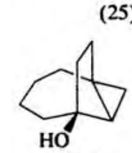
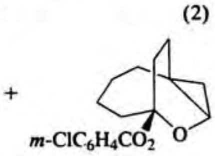
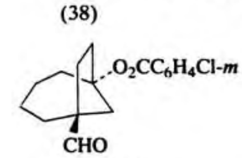
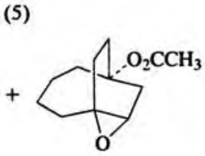
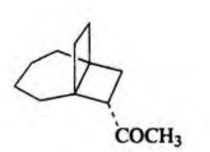
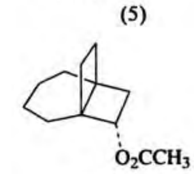
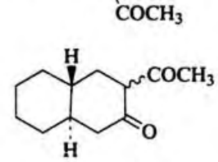
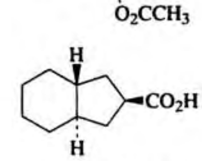
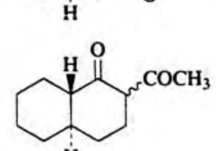
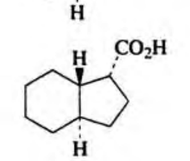
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4	 (>55)	57
$C_6H_5COCH_2N(C_2H_5)_2$	30% H_2O_2, CH_3OH, 30 min, 0°	$C_6H_5CO_2H$ (95)	73
	PBA, $CHCl_3$, 14 d, 25°	 (74)	98
	85% MCPBA, CH_2Cl_2, 64 h, 25°	 (77)	107
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 25°	 (90)	821
	MCPBA, CH_2Cl_2, 25°	 (5) +  (25) +  (2) +  (38) +  (5) +  (5) +  (2)	657, 804
	MCPBA, CH_2Cl_2, 25°	 (100)	657
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°	 (81)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°	 (92)	82

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

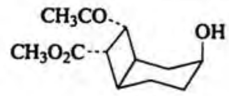
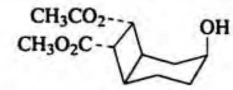
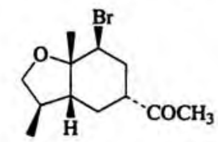
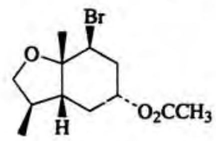
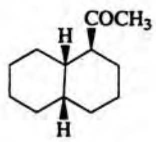
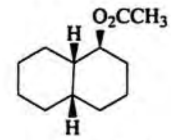
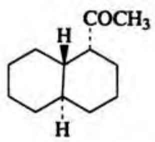
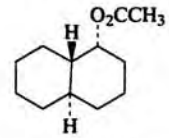
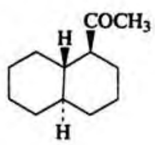
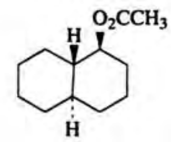
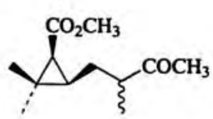
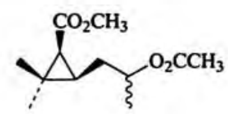
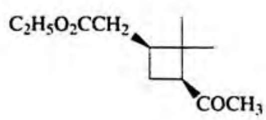
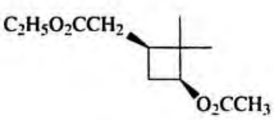
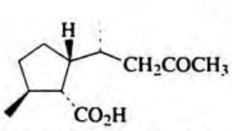
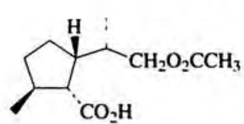
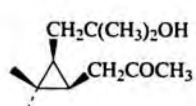
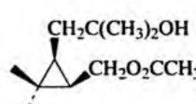
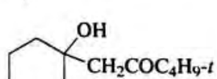
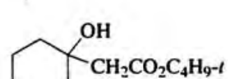
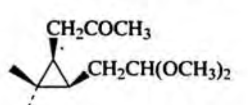
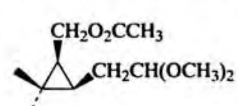
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 25°		(87)	822
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2.5 h, 25–30°		(92)	821
	77% PBA, $CHCl_3$, 12 d, 25°		(55)	823
	77% PBA, $CHCl_3$, 12 d, 25°		(72)	823
	77% PBA, $CHCl_3$, 12 d, 25°		(55)	823
	MCPBA, CH_2Cl_2, 6 h, heat		(65)	64
	PBA, $CHCl_3$, 15 d, 25°		(88)	692, 824
	TFPAA		(—)	825
$CH_3CO(CH_2)_8CH{=}CH_2$	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 9 h, 25°	$CH_3CO_2(CH_2)_8CH{=}CH_2$	(25)	220
	1. PBA, TsOH, $CHCl_3$, 6 h, 0° 2. 72 h, 10–15°		(80)	826
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat		(45)	86
$CH_3CO(CH_2)_6CO_2C_3H_7$-*i*	$K_2S_2O_8$, H_2SO_4, CH_3OH–H_2O, 5 h, 5–10°	$CH_3CO_2(CH_2)_6CO_2C_3H_7$-*i*	(89)	827
	70% MCPBA, CH_2Cl_2, 20 h, 20–30°		(75)	637, 638
C_{13}				
p-$FC_6H_4COC_6H_4F$-*p*	Na_2CO_4, CF_3CO_2H, 25°, 20 h	*p*-$FC_6H_4CO_2C_6H_4F$-*p*	(96)	763a
o-$ClC_6H_4COC_6H_4Cl$-*p*	40% PAA, H_2SO_4, 4–6 d, 25°	*o*-$ClC_6H_4CO_2C_6H_4Cl$-*p*	(80)	125
o-$ClC_6H_4COC_6H_5$	40% PAA, H_2SO_4, AcOH, 4–6 d, 25°	*o*-$ClC_6H_4CO_2C_6H_5$	(71)	125
$C_6H_5COC_6H_5$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat	$C_6H_5CO_2C_6H_5$	(88)	14, 42, 574, 734, 771, 828, 829, 830

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

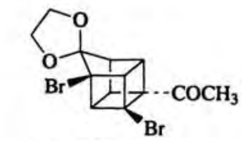
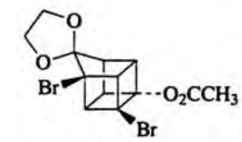
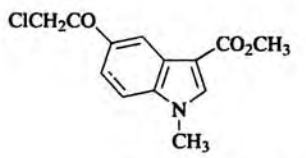
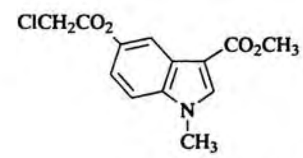
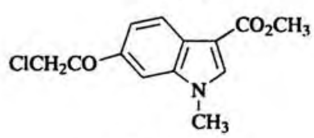
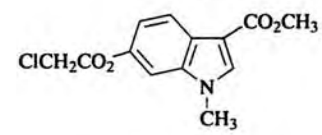
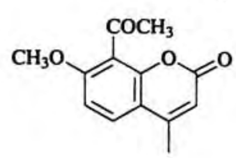
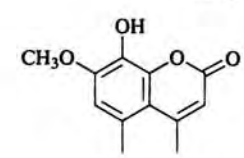
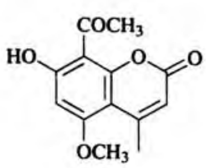
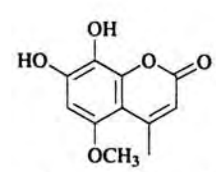
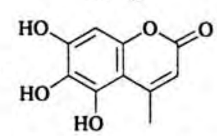
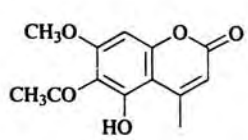
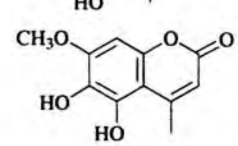
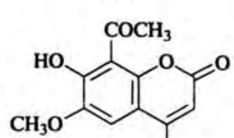
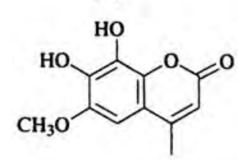
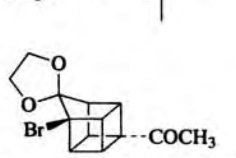
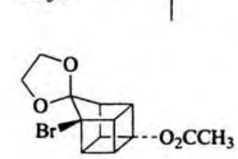
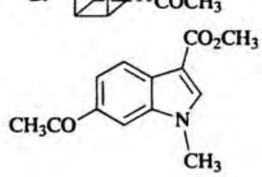
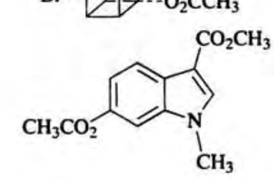
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA (2 eq, solid state, 24 h, 25°	"	(85)	740
	$NaBO_3$, TFAA, 4–8 h, 25°	"	(81)	114
o-$HOC_6H_4COC_6H_5$	30% H_2O_2, NaOH, 1.5 h	o-HOC_6H_4OH + $C_6H_5CO_2H$ (5) (11)	+(83)*	772
p-$HOC_6H_4COC_6H_5$	30% H_2O_2, NaOH, 1 h, 70°	$C_6H_5CO_2H$	(20) (73)*	772
	TFPAA		(59)	831
	MCPBA, Na_2HPO_4, CH_2Cl_2, 8 h, 20°		(22)	121
			(66)	
	30% H_2O_2, NaOH, 2.25 h, 5°		(73)	832
	30% H_2O_2, 4% NaOH, 2 h, 5°		(84)	832
	30% H_2O_2, 5% NaOH, 2.25 h, 5°		(—)	832
	30% H_2O_2, NaOH, pyridine, 2 h, 25°		(44)	832
	H_2O_2, NaOH, 1 h, 25°		(56)	815
	TFPAA (100%), Na_2HPO_4, CH_2Cl_2, 10 h, reflux		(94)	833, 834
	MCPBA, Na_2HPO_4, CH_2Cl_2, 1.5 h, 60°		(3)	121

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

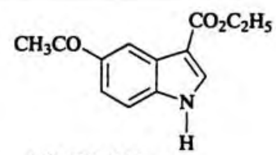
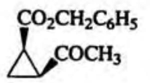
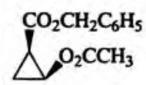
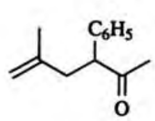
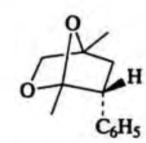
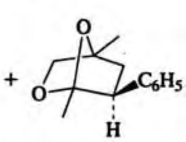
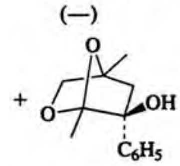
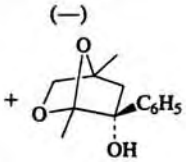
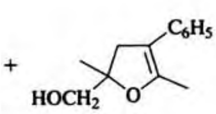
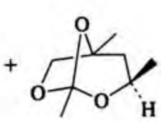
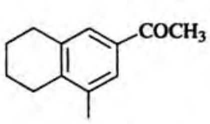
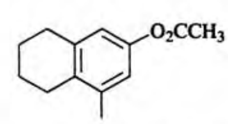
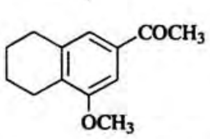
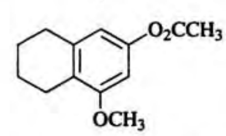
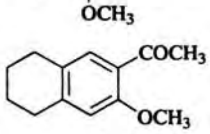
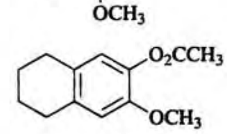
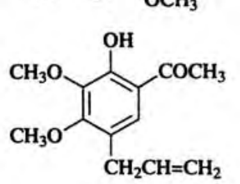
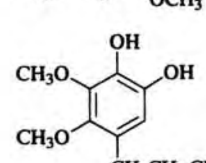
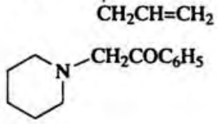
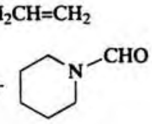
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA	(0)	835
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, reflux	 (25)	818
p-$O_2NC_6H_4COCH(NHCOCH_3)CH_2O_2CCH_3$	6% PAA, H_2SO_4, 10 h, 20°	p-$O_2NC_6H_4CO_2H$ (75)	74
D-$C_6H_5COCH(NHCOCH_3)CH_2O_2CCH_3$	6% PAA, H_2SO_4, 10 h, 20°	D-$HOCH_2CH(NH_2)CO_2H$ (64)	74
	MCPBA, CH_2Cl_2, 12 h, 25°	 (—) +  (—) +  (20) +  (10) +  (—) +  minor	634
$C_6H_5COC_6H_{11}$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, reflux	$C_6H_5O_2CC_6H_{11}$ (25) + $C_6H_5CO_2C_6H_{11}$ (75)	15, 836
	t-BuO_2H, KOH, 80°	$C_6H_5CO_2H$ (5) (90)*	532
	40% PAA, AcOH, 120 h, 25°	 (—)	837
	MCPBA, K_2CO_3, CH_2Cl_2, 41 h, 40°	 (47) (52)*	764
	MCPBA, CH_2Cl_2, 22 h, 25°	 (60)	764
	3% H_2O_2, NaOH, 2 h, 25°	 (50) (33)*	838
	30% H_2O_2, C_2H_5OH, 1–14 d	$C_6H_5CO_2H$ (14) +  (94)	73

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

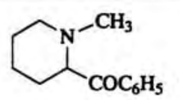
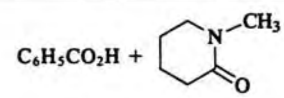
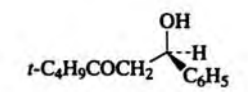
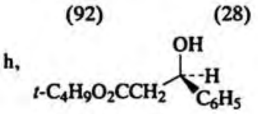
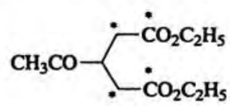
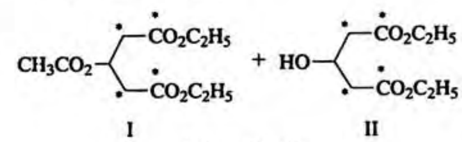
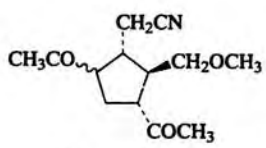
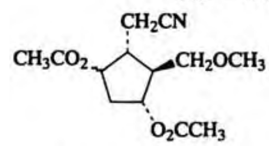
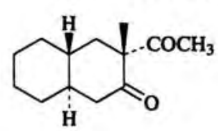
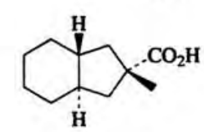
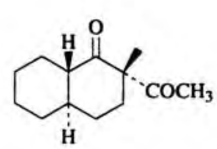
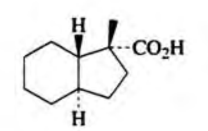
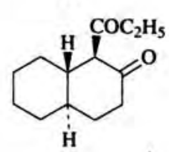
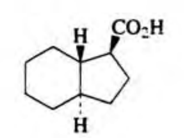
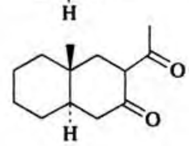
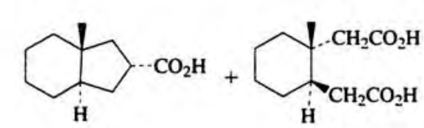
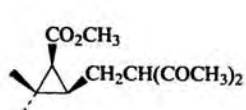
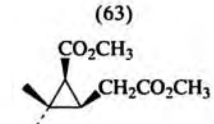
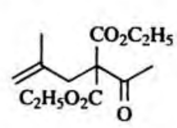
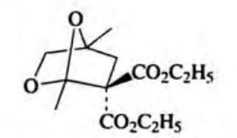
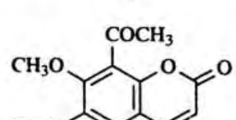
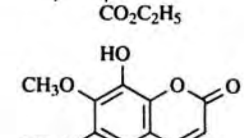
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, C_2H_5OH, 1–14 d	 (92) (28)		73
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, heat		(52)	86
 • = ^{13}C	TFPAA (90%), CH_2Cl_2, 24 h, heat	 I:II = 73:27	(73)	731
	TFPAA (90%), CH_2Cl_2, 20 min, heat, 2 h, 25°		(50)	839
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(91)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(93)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(—)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°	 (63) (14)		81
	1. 30% H_2O_2, NaOH, CH_3OH, 4 h, heat 2. CH_2N_2		(—)	77
	MCPBA, CH_2Cl_2, 1 h, heat		(—)	635
	30% H_2O_2, NaOH, 2 h, 0°		(89)	814

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

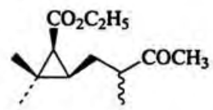
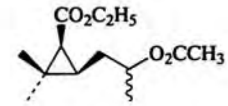
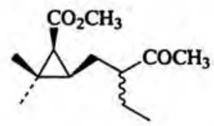
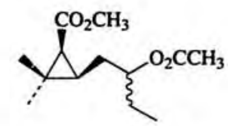
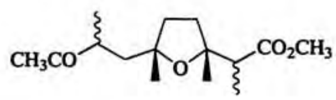
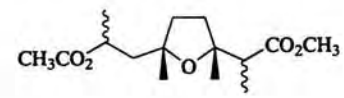
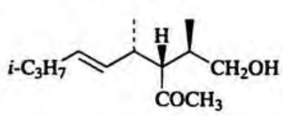
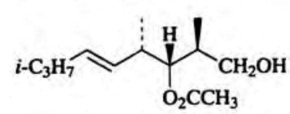
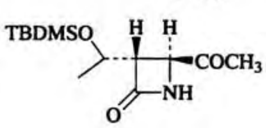
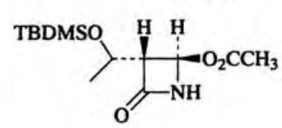
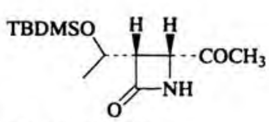
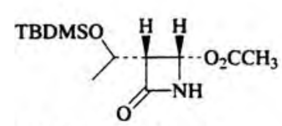
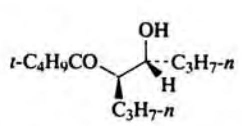
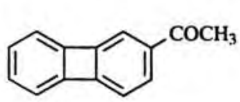
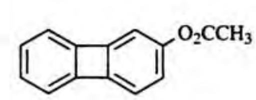
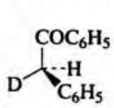
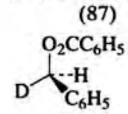
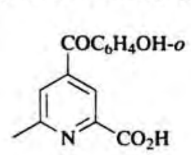
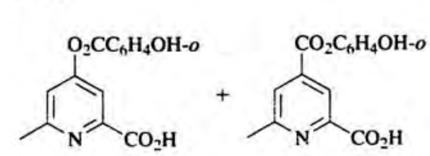
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PAA	 (75)	661
	MCPBA, CH_2Cl_2, 6 h, heat	 (64)	64
	TFPAA (80%), Na_2HPO_4, CH_2Cl_2, 12 h, reflux	 (76)	840
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, reflux	 (—)	841
	TFPAA, Na_2HPO_4, CH_2Cl_2, 5 d, 25°	 (—)	841
	H_2O_2, AcOH–THF	 (>82)	717
	80–90% MCPBA, $CHCl_3$, 4 d, 25°	 (84)	55, 842
	80–90% MCPBA, $CHCl_3$, 4 d, 25°	 (96)	55
n-$C_6H_{13}COC_6H_{13}$-n	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 5 h, 25°	n-$C_6H_{13}CO_2C_6H_{13}$-n (93)	220
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, reflux	(0)	86
C_{14}			
	36–40% PAA ($BaCO_3$ washed), AcOH, 20 h, 25°	 (84)	126
p-$HO_2CC_6H_4COC_6H_5$	30% H_2O_2, H_2SO_4, AcOH, 6.5 h, 40°	p-$HO_2CC_6H_4CO_2H$ (87) + C_6H_5OH (84)	843
	40% PAA, BF_3 etherate, 30 h, 45°	 (R) (—)	844
$C_6H_5COCH_2C_6H_4Cl$-p	t-BuO_2H, KOH, 80°	$C_6H_5CO_2H$ (I) + p-$ClC_6H_4CO_2H$ (II) (12) (80)*	532
		I:II = 50:50	
	H_2O_2 (0.1 M), NaOH, C_2H_5OH–H_2O, 4 h, 55°	I + II (85)	777
p-$ClC_6H_4COCH_2C_6H_5$	H_2O_2 (0.1 M), NaOH, C_2H_5OH–H_2O, 4 h, 55°	I + II (87)	777
	—	 mixture (—)	99

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

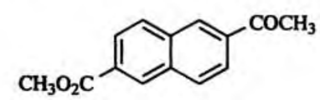
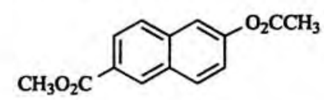
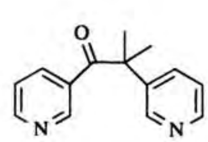
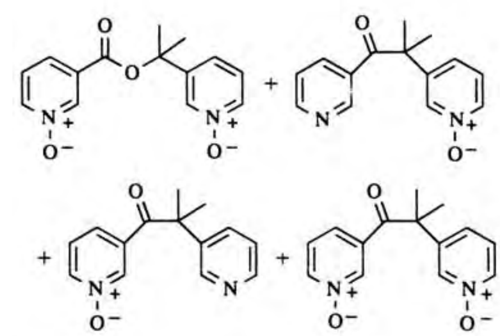
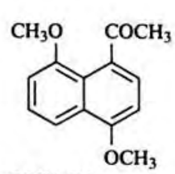
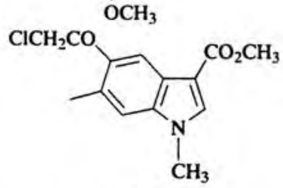
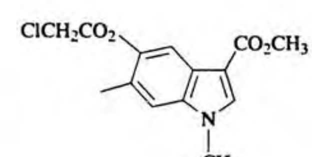
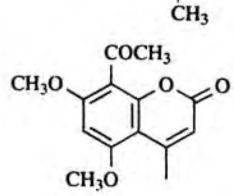
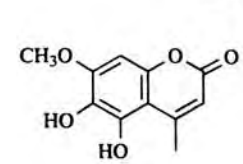
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
$p\text{-}C_6H_5C_6H_4COCH_3$	$NaBO_3$, TFAA–AcOH, 4–8 h, 25°	$p\text{-}C_6H_5C_6H_4O_2CCH_3$	(84)	114
$C_6H_5COCH_2C_6H_5$	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, heat	$C_6H_5CO_2CH_2C_6H_5$ (I) + $C_6H_5O_2CCH_2C_6H_5$ (II); I:II = 57:43	(90)	15
	MCPBA (2 eq), solid state, 24 h, 25°	I	(97)	532, 740
	$t\text{-}BuO_2H$, KOH, 80°	$C_6H_5CO_2H$	(12) (83)*	532
	H_2O_2 (0.22 M), NaOH, $C_2H_5OH\text{–}H_2O$, 6 h, 55°	$C_6H_5CO_2H$	(76)	777
$o\text{-}CH_3C_6H_4COC_6H_5$	40% PAA, H_2SO_4, AcOH, 4–6 d, 25°	$o\text{-}CH_3C_6H_4CO_2CC_6H_5$ I (38) + $o\text{-}CH_3C_6H_4O_2CC_6H_5$ II (12)		125
	MCPBA (2 eq), solid state, 4 d, 25°	I:II = 50:50	(39)	740
$p\text{-}CH_3C_6H_4COC_6H_5$	MCPBA (2 eq), solid state, 24 h, 25°	$p\text{-}CH_3C_6H_4O_2CC_6H_5$	(50)	740
$C_6H_5COCHOHC_6H_5$	70% MCPBA, CH_2Cl_2, 2–3 h, 0°	C_6H_5CHO	(90)	71
	$t\text{-}BuO_2H$, KOH, 80°	$C_6H_5CO_2H$	(16) +(80)*	532
$o\text{-}CH_3OC_6H_4COC_6H_5$	40% PAA, AcOH, 4–6 d, 25°	$o\text{-}CH_3OC_6H_4O_2CC_6H_5$	(82)	125
$p\text{-}CH_3OC_6H_4COC_6H_5$	40% PAA, AcOH, H_2SO_4 several d, 25°	$p\text{-}CH_3OC_6H_4O_2CC_6H_5$	(—)	14
$p\text{-}HOC_6H_4COC_6H_4CH_3\text{-}p$	30% H_2O_2, NaOH	$HO_2CC_6H_4CH_3\text{-}p$	(8) +(90)*	772
	PAA, AcOH, Amberlyst-15–sulfonic acid resin, 6 h, 75°		(47)	845
	MCPBA, $CHCl_3$, 1 h, 25°		(—)	100
	MCPBA or TFPAA		(0)	571
	MCPBA, Na_2HPO_4, $CHCl_3$, 6 h, 25°		(59)	120
	1. 4% NaOH, 3 h, heat 2. 30% H_2O_2, 2.25 h, 5°		(65)	676

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

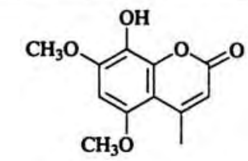
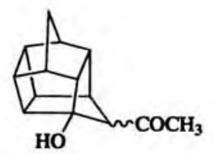
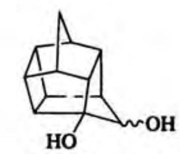
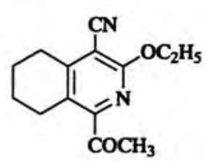
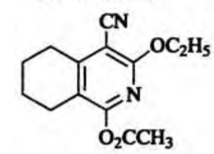
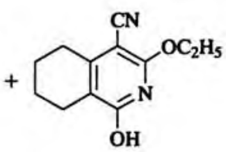
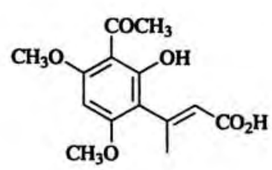
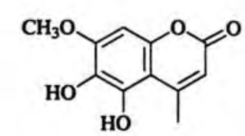
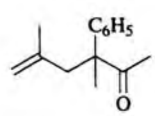
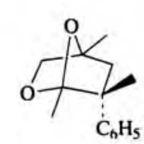
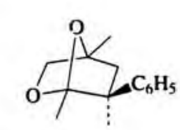
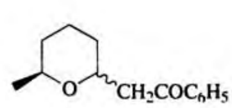
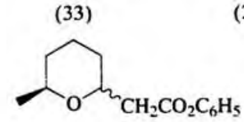
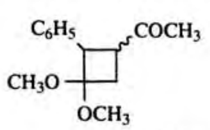
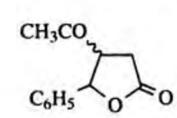
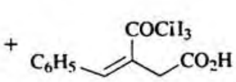
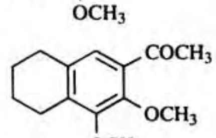
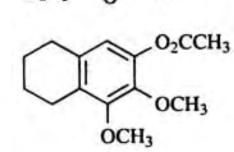
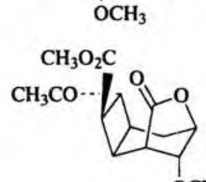
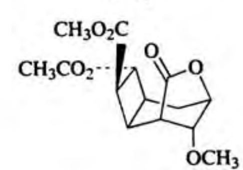
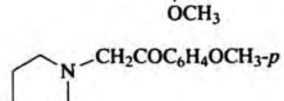
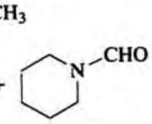
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, 4% NaOH, 2.25 h, 5°	 (33)	676, 832
	1. TFPAA (90%), CH_2Cl_2, 24 h, 25° 2. NaOH, CH_3OH, 17 h, 50°	 68:32 mixture (60)	54
	PBA, $CHCl_3$, 120 h, 25°	 (16) +  (38) +(21)*	846
	30% H_2O_2, NaOH, 2.25 h, 5°	 (74)	676, 832
	MCPBA, CH_2Cl_2, 2 h, 25°	 (33)  (22)	635
	TFPAA (100%), Na_2HPO_4, CH_2Cl_2, 3 h, 0°	 *cis* (94) *trans* (98)	112
	30% H_2O_2, AcOH, 6–7 h	 +  (95)	111
	MCPBA, CH_2Cl_2, 84 h, 40°	 (67)	764
	TFPAA (90%), Na_2HPO_4 CH_2Cl_2, 2 h, 25°	 (55)	67
	30% H_2O_2, C_2H_5OH, 1–14 d	p-$CH_3OC_6H_4CO_2H$ (92) +  (19)	73

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

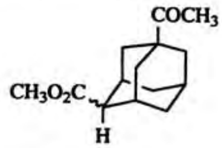
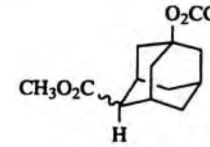
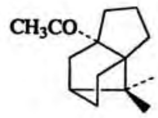
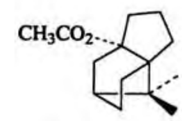
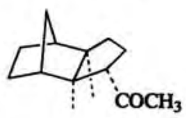
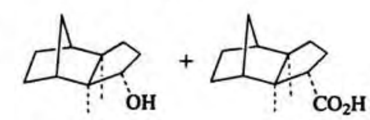
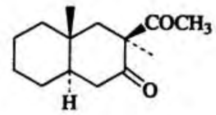
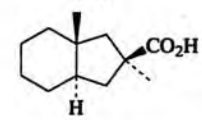
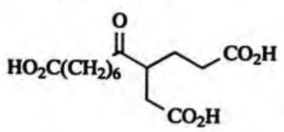
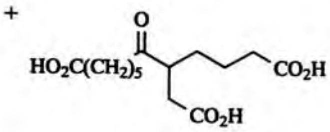
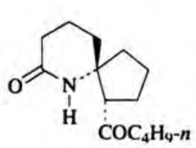
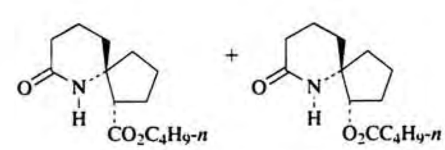
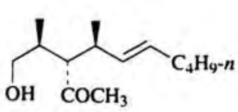
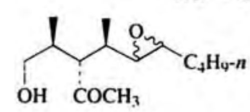
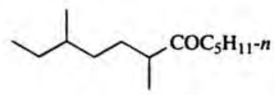
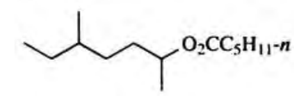
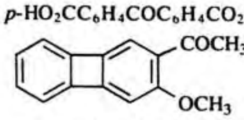
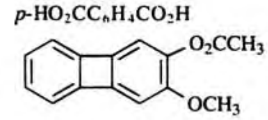
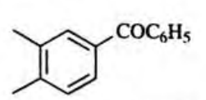
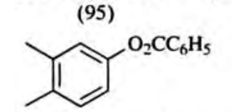
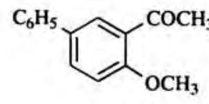
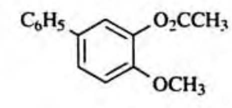
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 30 min, heat	 (66)	847
	—	 (—)	848
	TFPAA (80%), H_2SO_4, AcOH, 24 h, 25°	 (25) (34)	93
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°	 (73)	81
 + 	1. TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat 2. Hydrolysis and oxidation	$HO_2C(CH_2)_4CO_2H$ + $HO_2C(CH_2)_5CO_2H$ + $HO_2C(CH_2)_6CO_2H$ (—)	849
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, 25° 2. 2 h, reflux	 I + II (31) I:II = 53:47	92
	MCPBA	 (—)	110
	MCPBA, TsOH, $CHCl_3$, 92 h, 25°	 (90)	850
C_{15}			
p-$HO_2CC_6H_4COC_6H_4CO_2H$-*p*	H_2SO_5, H_2SO_4	*p*-$HO_2CC_6H_4CO_2H$ (50)	851
	15% PAA, H_2SO_4, AcOH, 4 h	 (—)	126
p-$CH_3C_6H_4COC_6H_4CH_3$-*p*	30% H_2O_2, H_2SO_4, AcOH, 11.5 h, 25°	*p*-$CH_3C_6H_4CO_2H$ (95) + *p*-$CH_3C_6H_4OH$ (95)	852
	40% PAA	 (76)	853
(*S*)-$C_6H_5CH(CH_3)COC_6H_5$	MCPBA, $ClCH_2CH_2Cl$, 72 h, 25°	(*S*)-$C_6H_5CH(CH_3)O_2CC_6H_5$ (—)	175
	15% PAA, H_2SO_4, AcOH, 80 h, 25°	 (50)	854

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

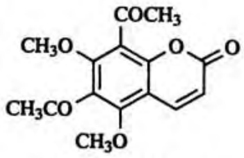
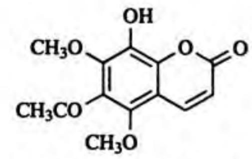
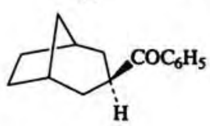
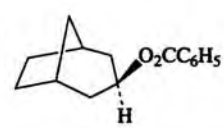
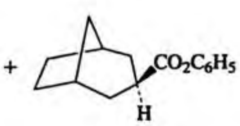
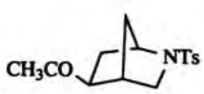
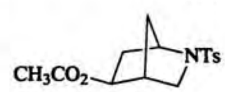
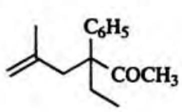
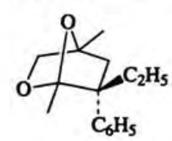
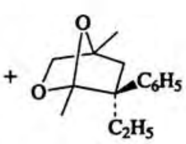
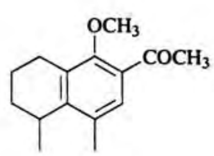
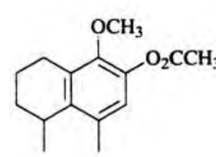
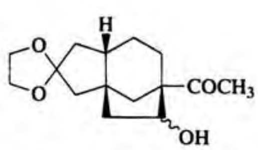
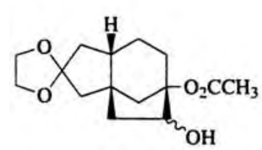
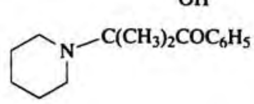
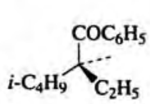
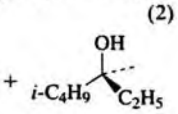
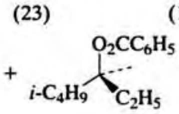
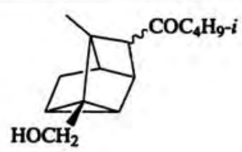
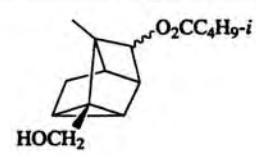
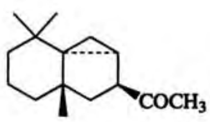
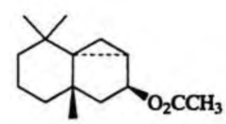
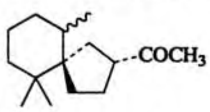
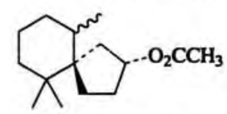
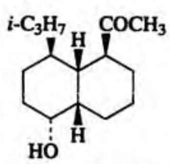
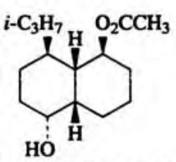
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6H_5CH(OCH_3)COC_6H_5$	70% MCPBA, CH_2Cl_2, 0°	$C_6H_5CHO + CH_3O_2CC_6H_5$ (—)	71
$C_6H_5C(CH_3)OHCOC_6H_5$	70% MCPBA, CH_2Cl_2, 2–3 d, 0°	No reaction (0)	71
	1. 6% H_2O_2, NaOH, 15 min, 0–5° 2. 2 h, 25°	 (56)	855
p-$CH_3CONHC_6H_4COCHCH_2O_2CCH_3$ NHCOCH3 (L)	6% PAA, H_2SO_4, 10 h, 20°	D-$HOCH_2CH(NH_2)CO_2H$ (D-Serine) (46)	74
	MCPBA, CH_2Cl_2, 8 d, 25°	 +  (81) I II I:II = 90:10	836
	MCPBA, CH_2Cl_2, 24 h, reflux	 (77)	856
	MCPBA, CH_2Cl_2, 2 h, 25°	 +  (45) (24)	635
	80–90% MCPBA, TsOH, CH_2Cl_2, 192 h, 5°	 (49)	857
	DNPBA, Na_2CO_3, TBP, $ClCH_2CH_2Cl$, 54°	 (71)	66
	30% H_2O_2, C_2H_5OH, 1–14 d	$C_6H_5CO_2H$ (96)	73
$C_6H_5COCH(CH_3)C_6H_{13}$-$n$	t-BuO_2H, KOH	$C_6H_5CO_2H$ (18) + $CH_3COC_6H_{13}$-n (11) + n-$C_6H_{13}CO_2H$ (2) + n-$C_5H_{11}CO_2H$ (2) +(57)*	124
 (*S*)	t-BuO_2H, KOH	$C_6H_5CO_2H$ (23) +  (*S*) (17) +  (*s*) (5) +(47)*	124

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2		(—)	858
	MCPBA, CH_2Cl_2		(—)	859
$HO_2C(CH_2)_4CHCO(CH_2)_4CO_2H$ with $CH_2CH_2CO_2H$ on CH	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	$HO_2C(CH_2)_4CO_2H$ (I) + $HO_2C(CH_2)_4OH$ (II); I:II = 83:17	(—)	849
$HO_2C(CH_2)_3CHCO(CH_2)_5CO_2H$ with $CH_2CH_2CO_2H$ on CH	TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 25°	$HO_2C(CH_2)_5CO_2H$ (I) + $HO_2C(CH_2)_5OH$ (II); I:II = 80:20	(—)	849
	PBA, $CHCl_3$, 140 h, 25°		(85)	860
	MCPBA, CH_2Cl_2, 8 d, 50°		(77)	62
$HO_2C(CH_2)_6CO(CH_2)_6CO_2H$	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	$HO_2C(CH_2)_6CO_2H$ (I) + $HO_2C(CH_2)_6OH$ (II); I:II = 50:50	(67)	861

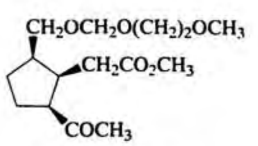
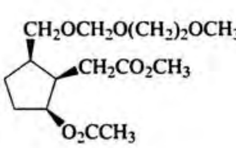
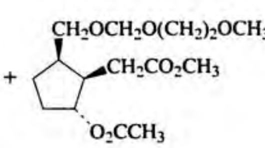
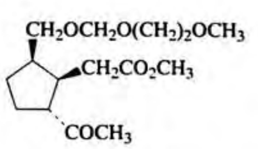
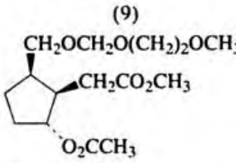
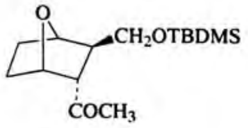
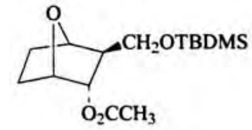
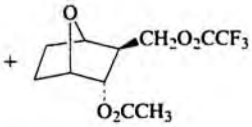
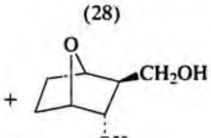
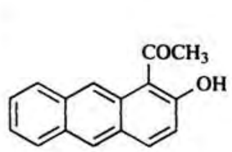
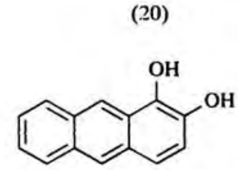
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	80% MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°	 (9) +  (42)		83
	80% MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°		(78)	83
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 6.5 h, 0°	 (28) +  (25) +  (20)		58
C_{16}				
	15% H_2O_2, NaOH, pyridine, 1.5 h, 25°		(84)	568

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

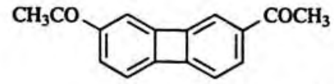
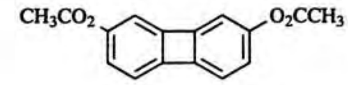
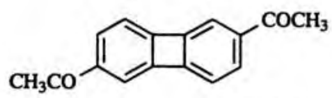
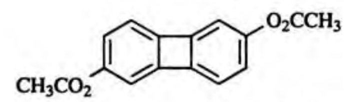
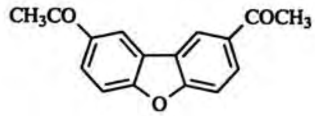
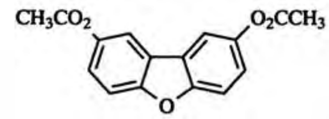
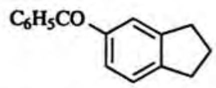
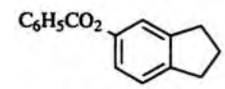
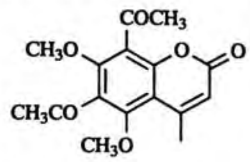
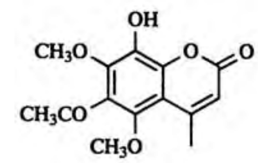
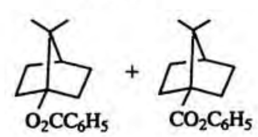
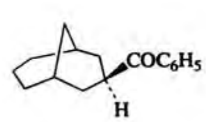
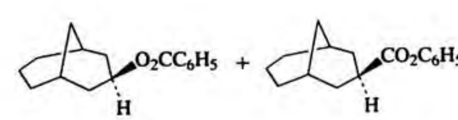
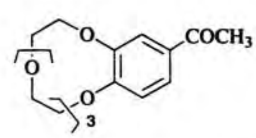
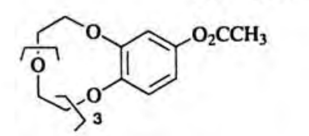
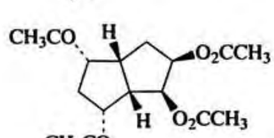
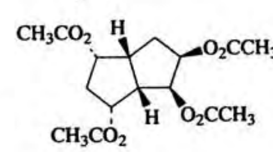
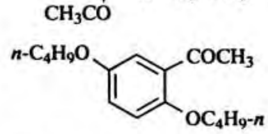
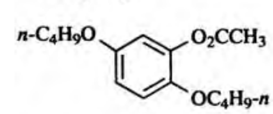
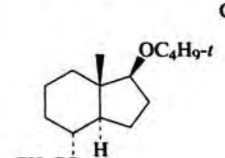
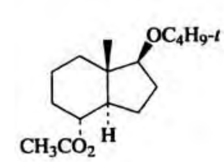
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, H_2SO_4, AcOH, 3 h, 35–40°		(23)	126
	36–40% PAA, H_2SO_4, AcOH, 6 h, 35°		(60)	126
	MCPBA, $CHCl_3$, 4 d, 25°		(88)	862
	40% PAA		(85)	853
p-(i-C_3H_7O)$C_6H_4COC_6H_5$	11% PAA, H_2SO_4, AcOH, 96 h, 25°	p-(i-C_3H_7O)$C_6H_4O_2CC_6H_5$	(92)	798
	1. 6% H_2O_2, NaOH, 0–10°, 15 min 2. 2 h, 25°		(33)	855
	TFPAA (88%), Na_2HPO_4, CH_2Cl_2, 1 h	 I II I:II = 97.5:2.5	(90)	15
	MCPBA, CH_2Cl_2, 8 d, 25°	 I II I:II = 92:8	(85)	836
	9% PAA, AcOH, 5.5 h, 30–32°		(82)	863
	MCPBA, CH_2Cl_2, 13 d, reflux		(54)	864
	PAA, NaOAc, AcOH, 12 h, 40–42°		(50)	788
$HO_2C(CH_2)_4CO(CH_2)_4CHCO_2H$ (CH bearing $CH_3CO(CH_2)_2$)	1. TFPAA 2. NaOH, CH_3OH	$HO_2C(CH_2)_4CO_2H$ + $HO_2C(CH_2)_4OH$	(—)	849
	MCPBA, CH_2Cl_2, 25°		(95)	105

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

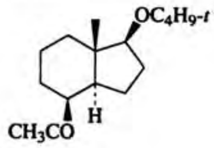
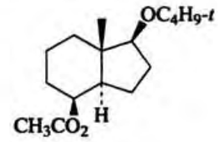
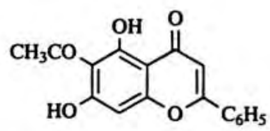
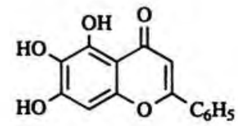
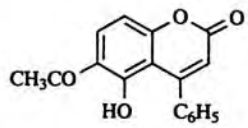
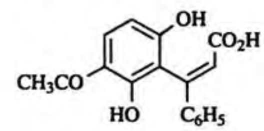
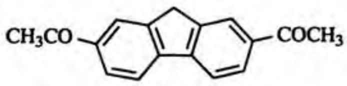
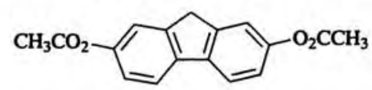
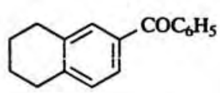
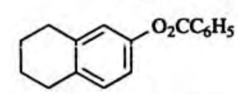
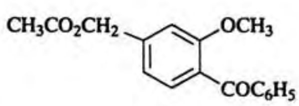
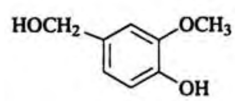
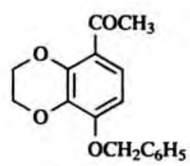
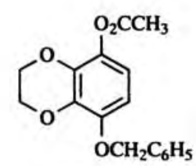
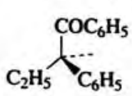
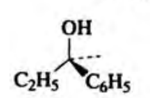
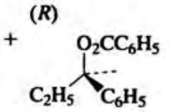
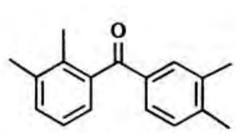
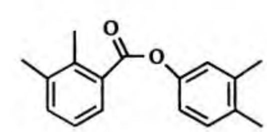
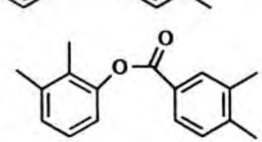
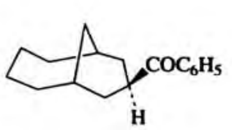
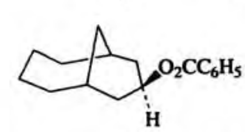
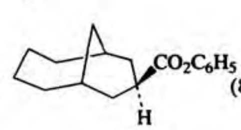
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, 0° 2. 30 h, 25°	 (57)	59
C_{17}			
	30% H_2O_2, NaOH, 12 h, 0°	 (66)	865
	30% H_2O_2, 5% NaOH, 2.25 h, 0°	 (—) no oxidation	866
	MCPBA, TFAA, $CHCl_3$, 3 d, 25°	 (62)	867
	40% PAA	 (85)	853
	8% PAA, H_3PO_4, AcOH, 72 h, 25°	 (42)	798
	36% H_2O_2, HCO_2H, 72 h, 0°	 (89)	868
	*t*-BuO_2H, KOH, 50°	 (*R*) (13) +  (*R*) (9) + $C_6H_5CO_2H$ (65) (20)*	124
	40% PAA	 +  (80–85)	853
	MCPBA, CH_2Cl_2, 8 d, 25°	 I +  II (82) I:II = 90:10	836

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

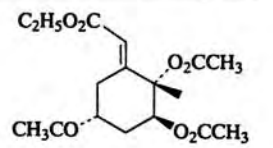
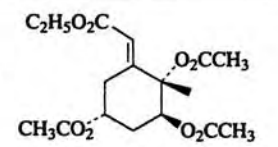
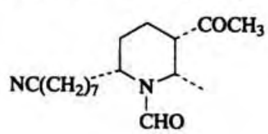
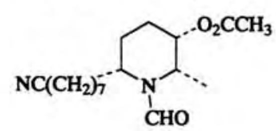
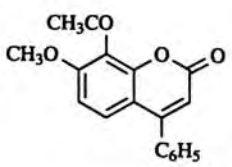
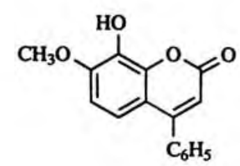
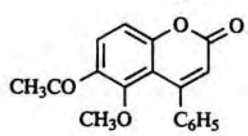
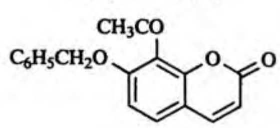
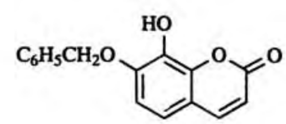
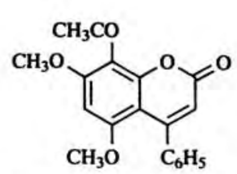
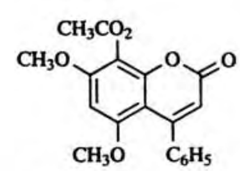
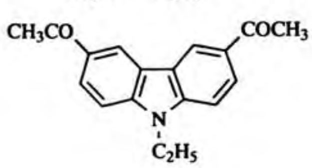
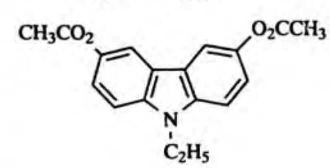
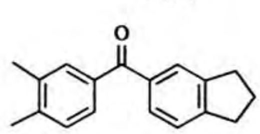
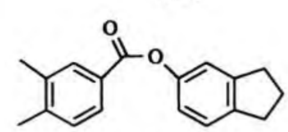
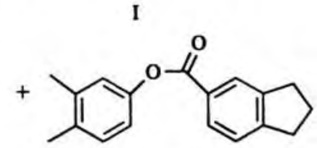
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, NaH_2PO_4, CH_2Cl_2, 0°		(>75)	105
	TFPAA, Na_2HPO_4, CH_2Cl_2		(71)	869
C_{18}				
	30% H_2O_2, NaOH, 2.25 h, 5°		(66)	832
	30% H_2O_2, 5% NaOH, 2.25 h, 0°		(0)	866
	30% H_2O_2, NaOH, 2.25 h, 5°		(77)	870
	30% H_2O_2, NaOH, 2.25 h, 10–15°		(43)	871
	90% MCPBA, $CHCl_3$, 4 d, 25°		(70)	862
	40% PAA	 I +  II I:II = 52–55:45–48	(—)	853
p-$CH_3OC_6H_4COCH_2CHCH_2C_6H_5$ (with CO_2H on CH)	MCPBA, $CHCl_3$, 3 d, 25°	p-$CH_3OC_6H_4O_2CCH_2CHCH_2C_6H_5$ (with CO_2H on CH)	(57)	872

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

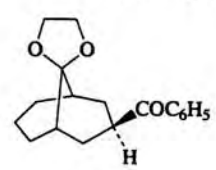
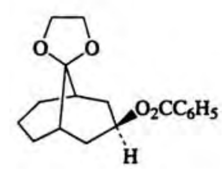
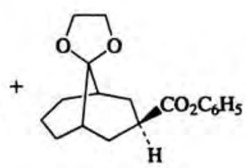
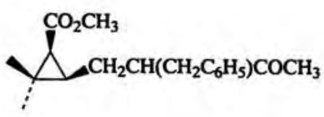
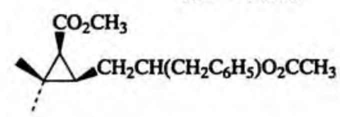
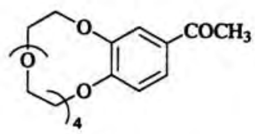
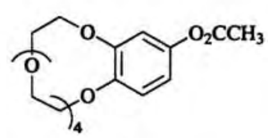
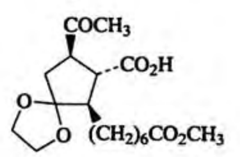
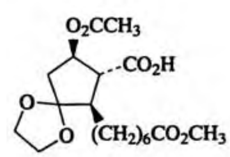
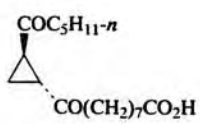
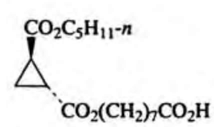
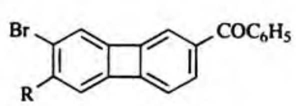
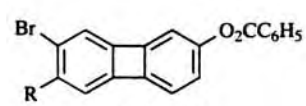
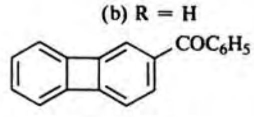
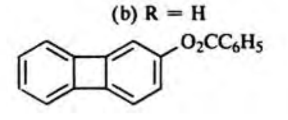
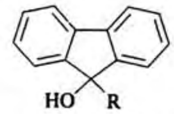
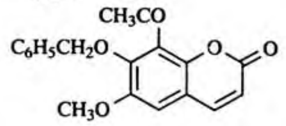
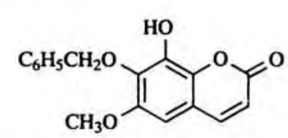
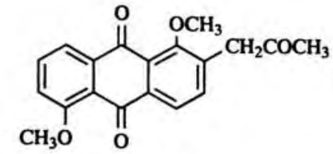
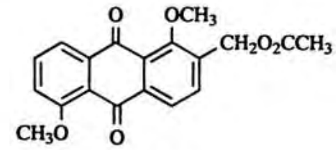
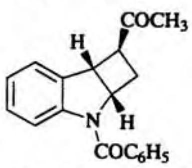
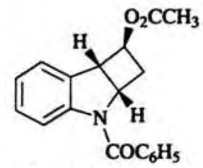
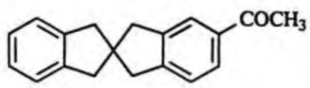
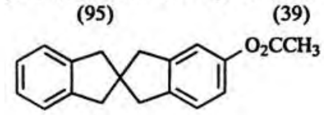
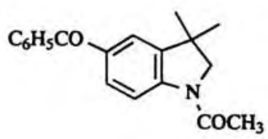
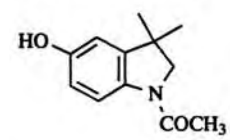
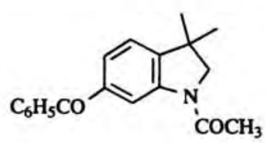
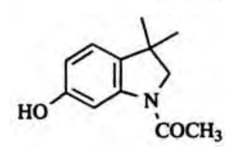
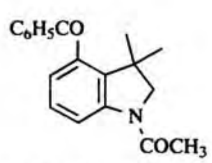
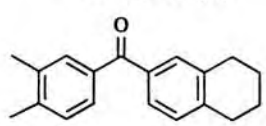
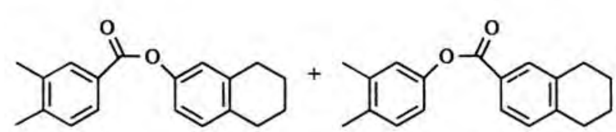
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
$C_6H_5COCH(NHCO_2CH_2C_6H_5)CH_2O_2CNH_2$	6% PAA, H_2SO_4, 10 h, 20°	$C_6H_5CO_2H$	(61)	74
	MCPBA, CH_2Cl_2, 25°	 I +  II I:II = 90:10	(—)	444
	MCPBA, CH_2Cl_2, 6 h, heat		(59)	64
	9% PAA, AcOH, 5.5 h, 30–32°		(65)	863
	TFPAA, Na_2HPO_4		(95)	873
	TFPAA, Na_2HPO_4, CH_2Cl_2, 25°		(87)	874
C_{19}				
 (a) R = Br (b) R = H	36–40% PAA, H_2SO_4, AcOH, 52 h, 40–42°	 (a) R = Br (b) R = H	 (24) (44)	875
	36–40% PAA, AcOH, 8 h, 35°		(61)	127, 875
 (a) R = *p*-ClC_6H_4 (b) R = C_6H_5	30% H_2O_2, AcOH, H_2SO_4, 25°	*o*-[*o*-HOC_6H_4]$C_6H_4O_2CR$ (a) R = *p*-ClC_6H_4 (b) R = C_6H_5	 (40) (27–39)	723
	30% H_2O_2, NaOH, 2.25 h, 5°		(76)	832

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2, 3 h, 25°	 (—)	876
	MCPBA, CH_2Cl_2, 12 h, 25°	 (92)	56
p-$C_2H_5O_2CC_6H_4COC_6H_4CO_2C_2H_5$-*p*	H_2O_2, H_2SO_4, AcOH	*p*-$HO_2CC_6H_4CO_2H$ (95) + *p*-$HO_2CC_6H_4OH$ (39)	851
	MCPBA, $NaHCO_3$, $CHCl_3$, 3 d, 25°	 (58)	877
	—	 (—)	878, 879
	—	 (—)	878, 879
	—	(0)	878, 879
$C_6H_5COCH(NHCO_2CH_2C_6H_5)CH_2O_2CCH_3$	PAA, H_2SO_4, 10 h, 20°	$C_6H_5CO_2H$ (67)	74
	40% PAA	 (—)	853

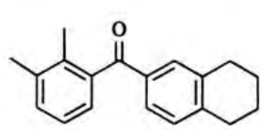
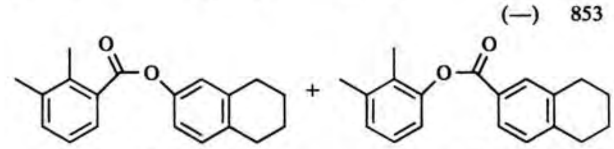
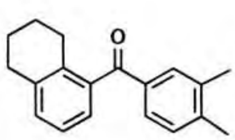
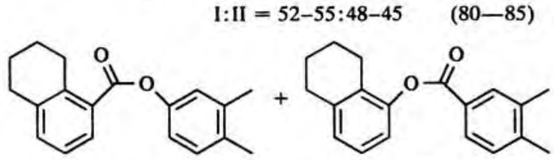
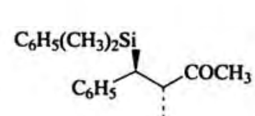
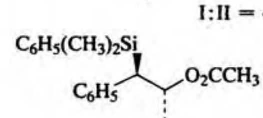
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	40% PAA	 I, II; I:II = 52–55:48–45 (80—85)	853
	40% PAA	 I, II; I:II = 45–48:52:55 (80–85)	853
	MCPBA, Na_2HPO_4, CH_2Cl_2, 24 h, 25°	 (96)	880, 881

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

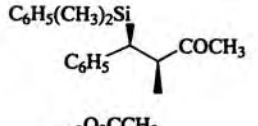
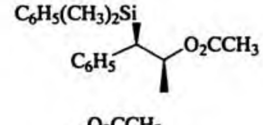
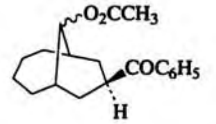
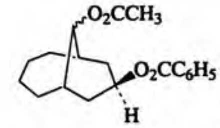
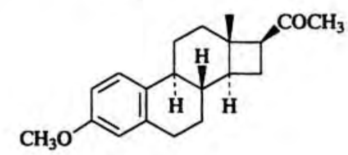
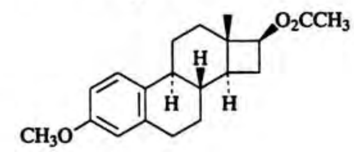
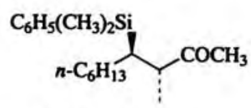
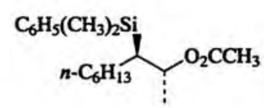
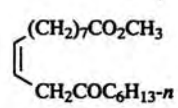
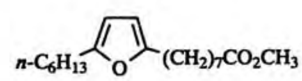
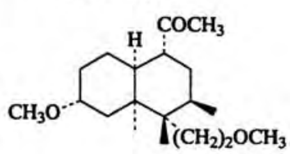
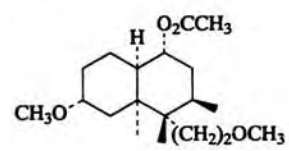
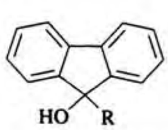
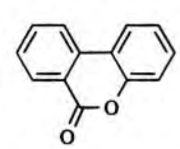
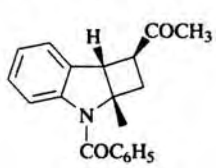
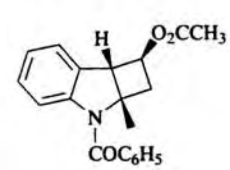
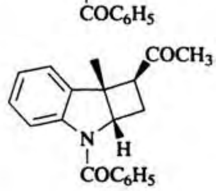
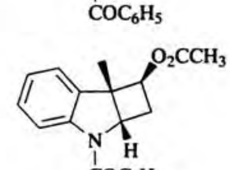
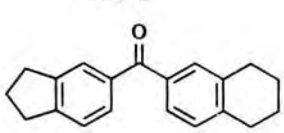
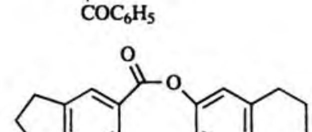
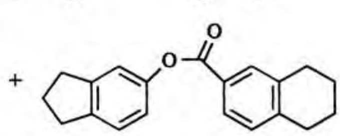
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, Na_2HPO_4, CH_2Cl_2, 24 h, 25°		(95)	880, 881
	MCPBA, CH_2Cl_2, 3 h, 25°		(92)	444
	10% MPPA, ether, 30 d, −3°		(85)	747
	MCPBA, Na_2HPO_4, CH_2Cl_2		(42)	880
	MCPBA, $NaHCO_3$, $CHCl_3$, 24 h, 25°		(25)	103
	TFPAA		(>55)	271
C_{20}				
	30% H_2O_2, AcOH, H_2SO_4, 25°	 + o-[o-HOC_6H_4]$C_6H_4O_2CR$		723
(a) R = p-$CF_3C_6H_4$		(a) R = p-$CF_3C_6H_4$ (—) (45)		
(b) R = p-$CH_3C_6H_4$		(b) R = p-$CH_3C_6H_4$ (3.5) (65)		
(c) R = p-$CH_3OC_6H_4$		(c) R = p-$CH_3OC_6H_4$ (31) o-(o-HOC_6H_4)$C_6H_4CO_2R$ (3)		
	MCPBA, CH_2Cl_2, 20 h, heat		(23) (46)*	882
	MCPBA, CH_2Cl_2, 20 h, heat		(58)	882
	40% PAA	 + 	(-)	853

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

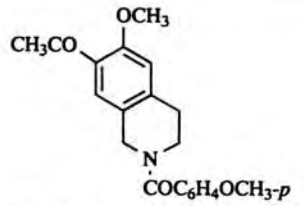
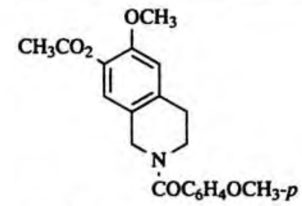
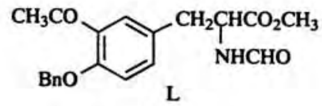
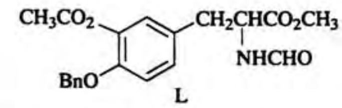
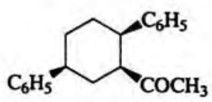
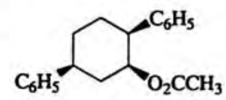
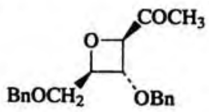
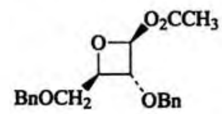
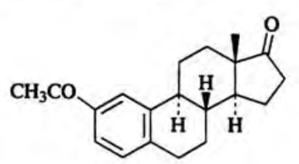
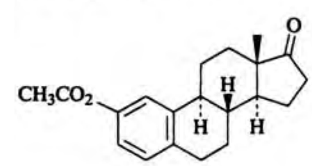
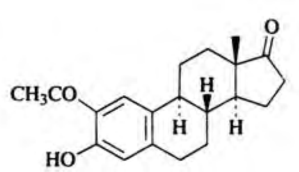
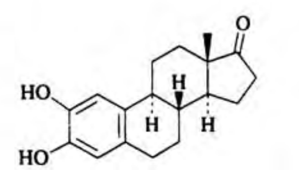
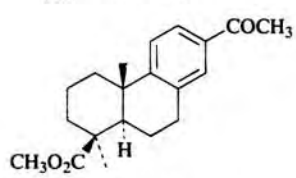
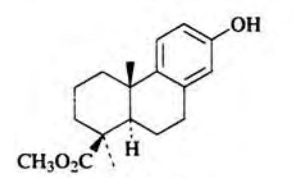
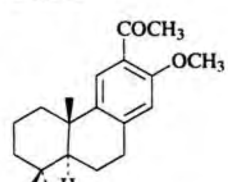
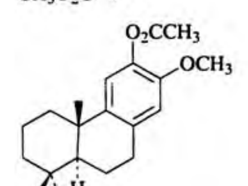
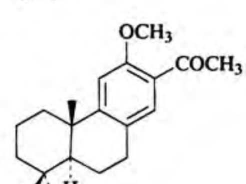
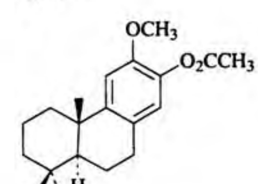
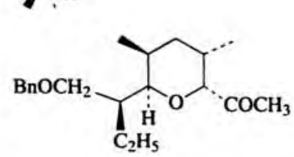
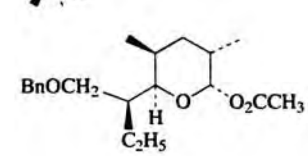
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, 89 h, 25°		(62)	764
	MCPBA, $CHCl_3$, 48 h, reflux		(33) (33)*	883
	85% MCPBA, $CHCl_3$, 9 d, 25°		(93)	884
	MCPBA, CH_2Cl_2, 48 h, 4°		(97)	885
	PBA, $CHCl_3$, 7 d, 25°		(68)	118
	3% H_2O_2, NaOH (pH 8.2–8.5), 5 h, 12°		(93)	119
	MCPBA, CH_2Cl_2, 0°		(68)	886
	40% PAA, CH_2Cl_2, 42 h, 25°		(92)	887
	40% PAA, CH_2Cl_2, 60 h, 25°		(31)	887
	MCPBA, Na_2HPO_4, CH_2Cl_2, 25°		(90)	61

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

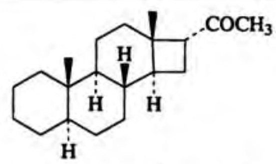
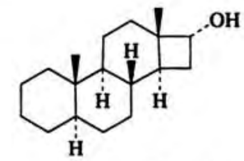
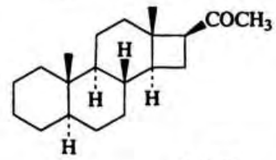
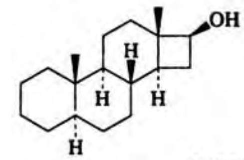
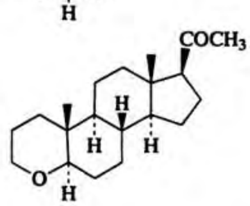
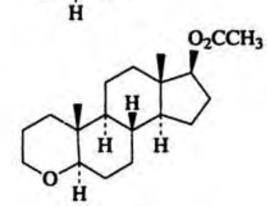
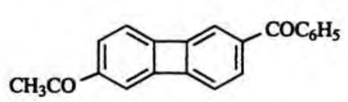
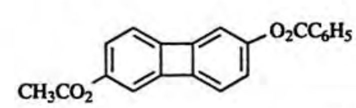
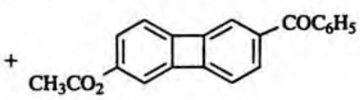
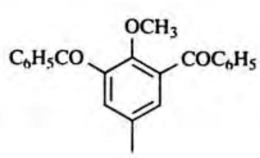
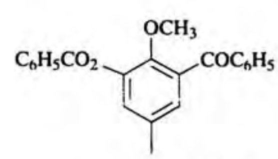
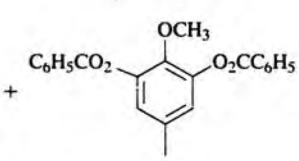
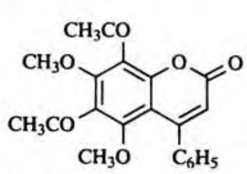
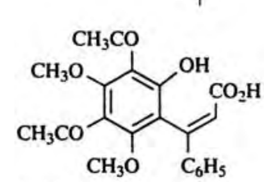
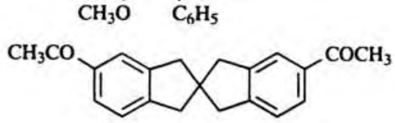
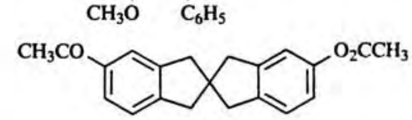
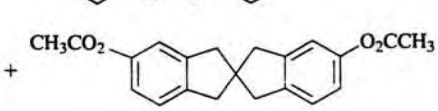
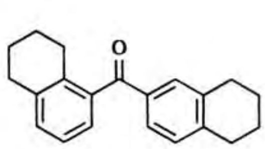
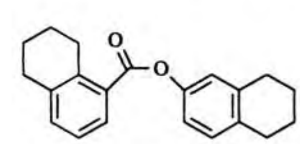
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, TsOH, CH_2Cl_2, 72 h, 25°	 (18)	888
	MCPBA, TsOH, CH_2Cl_2, 72 h, 25°	 (84)	888
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1.75 h	 (86)	507
C_{21}			
	1. PAA, H_2SO_4, AcOH, 4 h, 35° 2. 12 h, 0°	 (18)	126
		+  (21)	
	86% MCPBA, TFAA, 2–4 d, 25°	 (12–15)	798
		+  (12–15)	
	30% H_2O_2, NaOH, 2.25 h, 0°	 (77)	866
	MCPBA, $NaHCO_3$, $CHCl_3$, 1 d, 25°	 (20)	877
		+  (41)	
	40% PAA	 (80–85)	853

TABLE I. Reactions of Straight-Chain Ketones (*Continued*)

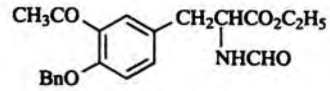
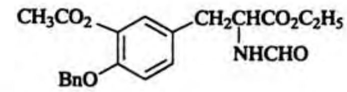
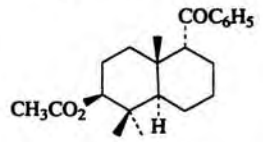
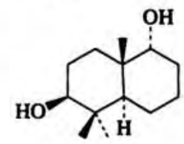
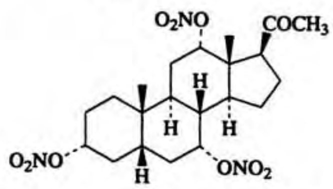
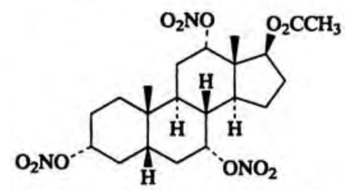
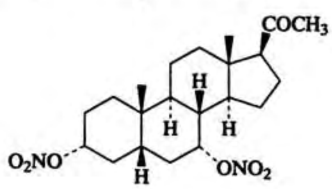
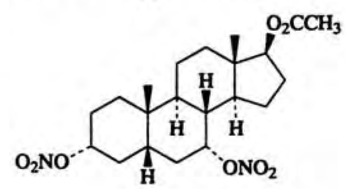
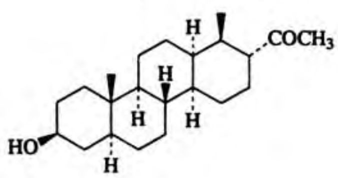
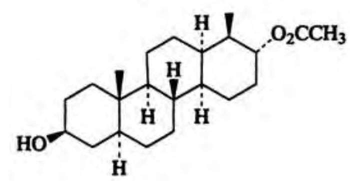
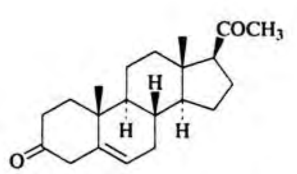
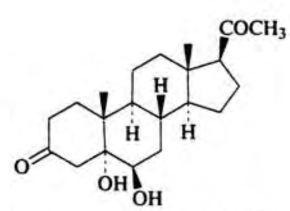
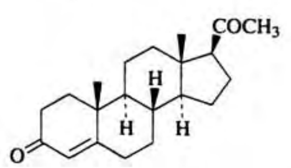
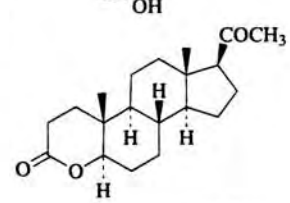
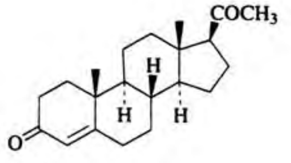
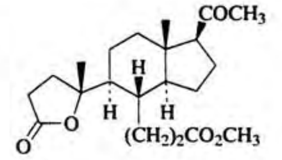
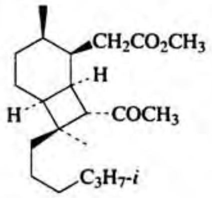
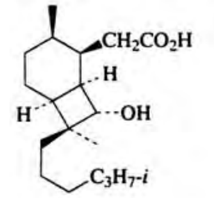
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $CHCl_3$, 48 h, reflux		(36) (19)[a]	883
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 8 d, 25°		(91)	730
	TFPAA (90%), K_2HPO_4, $CHCl_3$, 12 h, heat		(89)	889
	PBA, $CHCl_3$, 12 d, 25°		(68)	890
	83% PBA, $CHCl_3$, 157 h, 25°		(100)	891
	50% H_2O_2, SeO_2, t-C_4H_9OH, 7 h, heat		(69)	101
	K_2SO_5, H_2SO_4, AcOH, 3 d		(21)	507
	1. 50% H_2O_2, SeO_2, t-C_4H_9OH, 7 h, reflux 2. CH_2N_2		(33)	101
	MCPBA, TsOH, CH_2Cl_2, 24 h, 25°		(68)	892

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

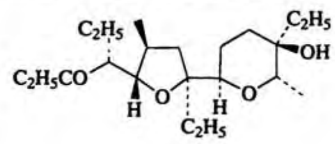
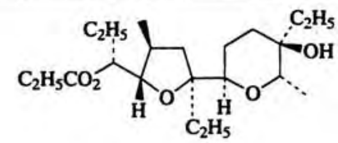
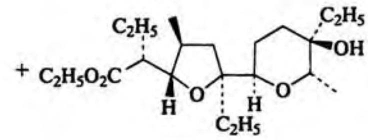
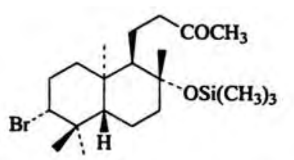
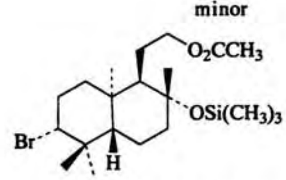
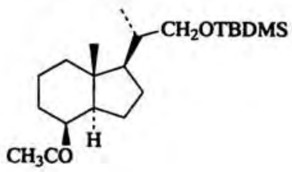
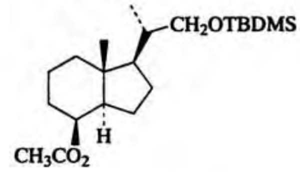
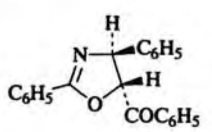
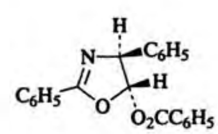
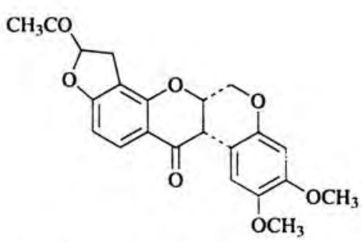
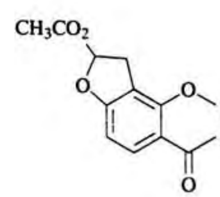
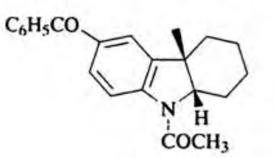
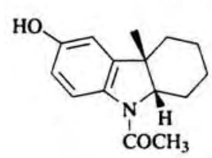
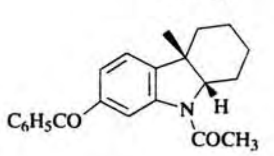
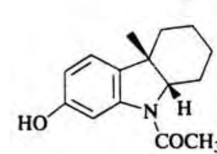
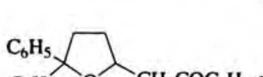
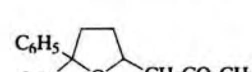
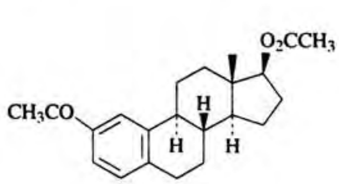
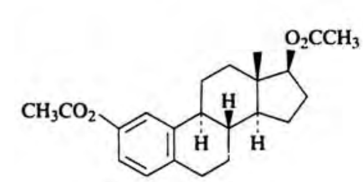
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 25°	 major +  minor (—)	80
	MCPBA, $CHCl_3$, 10 d, 25°	 (75)	893
	MCPBA, CH_2Cl_2, 25°	 (95)	60
C_{22}			
	MCPBA, CH_2Cl_2, 12 h, 25°	 (80)	69
	MCPBA	 (—)	70
	—	 (—)	878, 879
	—	 (—)	878, 879
	1. 30% H_2O_2, AcOH, 120 h, 50–60° or 70% H_2O_2, AcOH, 96 h, 40–50° 2. CH_3OH, H_2SO_4, 4 h, heat	 (26)	84
	PBA, $CHCl_3$, 7 d, 25°	 (88)	118

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

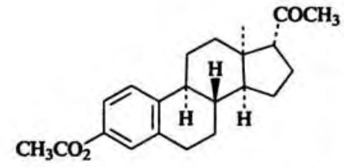
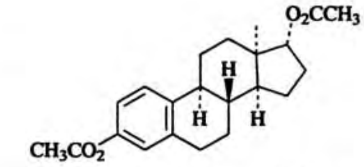
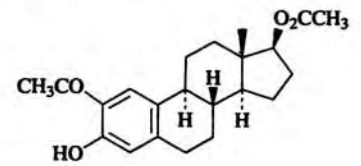
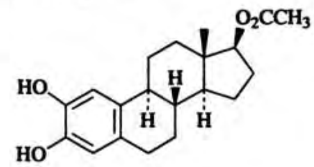
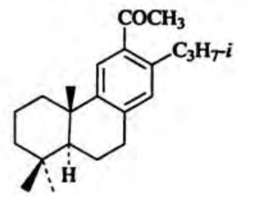
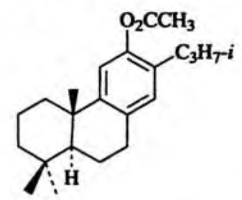
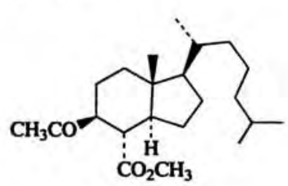
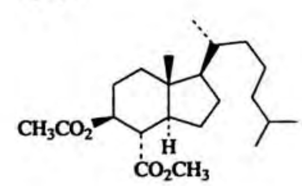
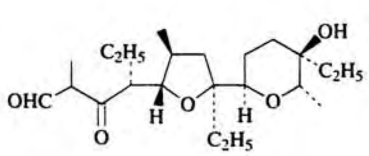
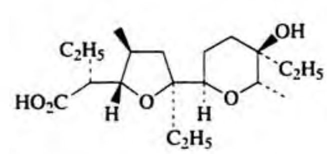
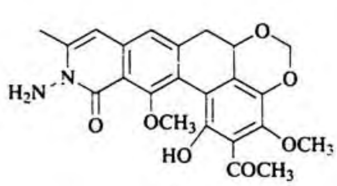
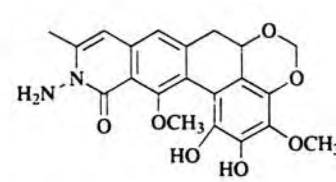
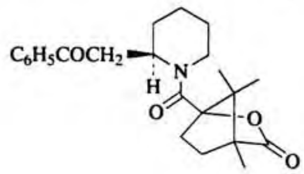
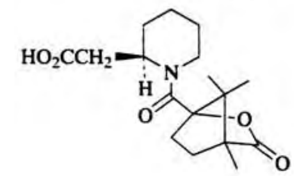
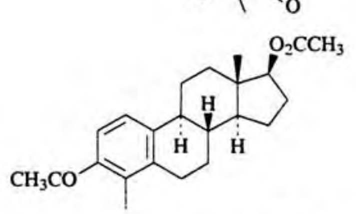
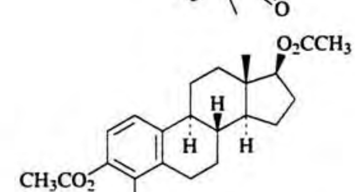
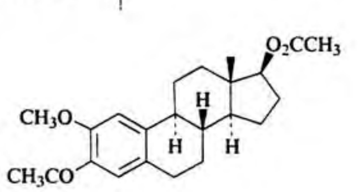
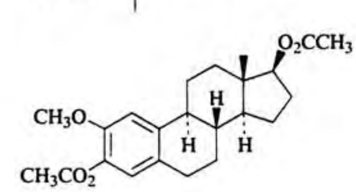
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 30 h, 35°	 (38)	894
	6% H_2O_2, NaOH (pH 8.2–8.5), diglyme, 30 h	 (85)	119
	40% PAA, CH_2Cl_2, 72 h, 25°	 (100)	887
	TFPAA (85%), Na_2HPO_4, CH_2Cl_2, 30 min, reflux	 (80)	895
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, several min	 (79)	80
C_{23}			
	H_2O_2, NaOH, CH_3OH–dioxane, 25 min, 20°	 (31)	896
	TFPAA, 0–20°	 (88)	897
	MCPBA, $CHCl_3$, 10 d, 25°	 (26)	898
	PBA, $CHCl_3$, 13 d, 25°	 (60)	118

TABLE I. Reactions of Straight-Chain Ketones (*Continued*)

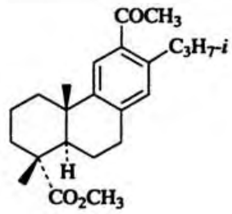
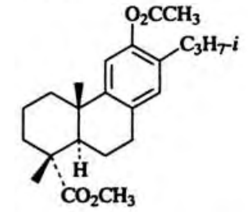
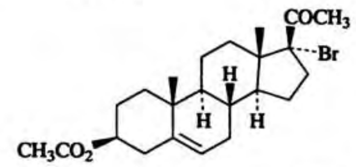
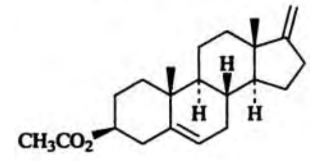
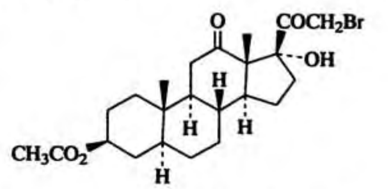
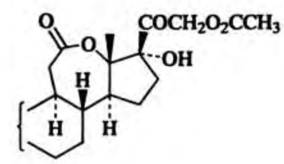
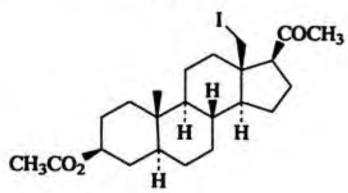
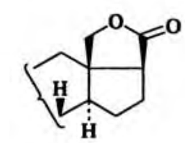
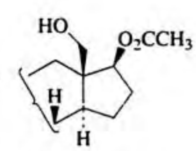
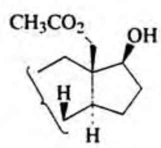
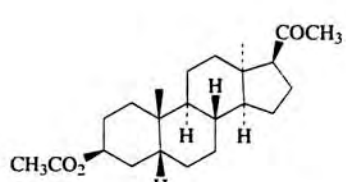
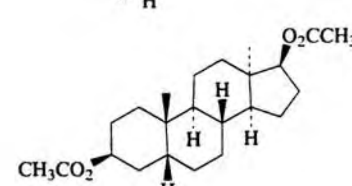
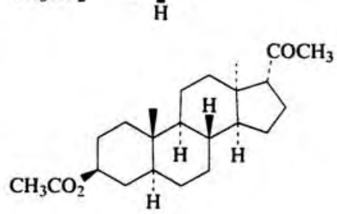
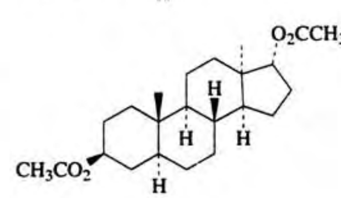
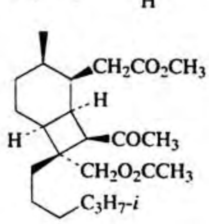
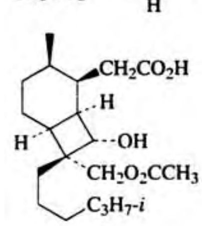
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	3,5-DNPBA, CH_3SO_3H, CH_2Cl_2, 25°		(—)	899
	50% H_2O_2, NaOH, *t*-C_4H_9OH, reflux		(65)	672
	PBA, H_2SO_4, AcOH, $CHCl_3$, 92 h, 25°		(36)	282
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, −5 to 25°		(25)	91
		+ 	(25)	
		+ 	(25)	
	MCPBA, $CHCl_3$, 25 h, 35°		(48)	900
	MCPBA, $CHCl_3$, 30 h, 35°		(64)	900
	MCPBA, TsOH, $CHCl_3$, 48 h, heat		(48)	892

TABLE I. Reactions of Straight-Chain Ketones (*Continued*)

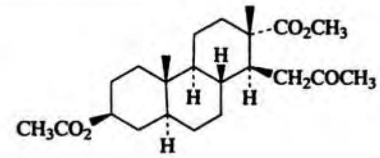
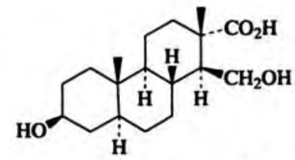
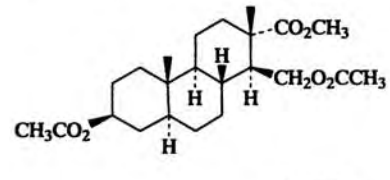
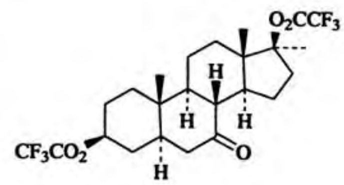
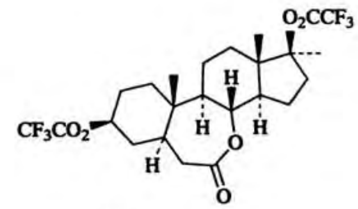
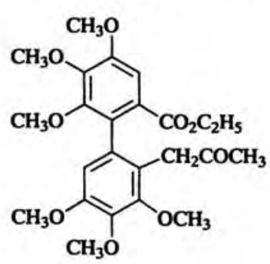
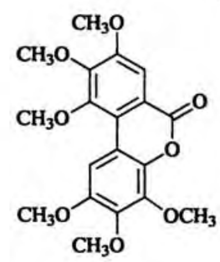
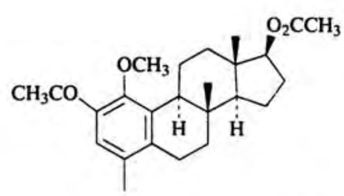
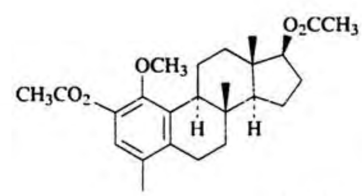
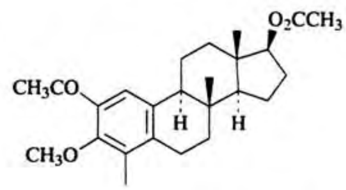
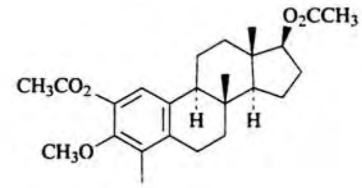
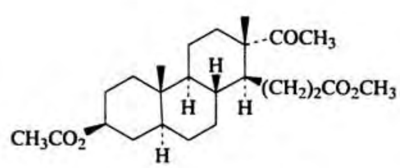
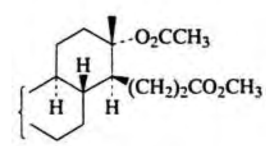
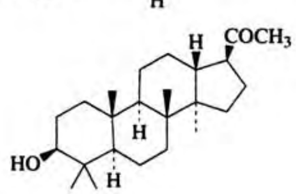
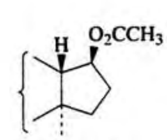
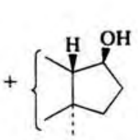
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2.5 h, 25° 2. Hydrolysis		(40)	901
	PBA, benzene, 8 d, 25°		(—)	902
C_{24}				
	MCPBA, $CHCl_3$, 4 h, reflux		(99)	903
	MCPBA, H_2SO_4, CH_2Cl_2, 3 d, 0°		(5)	320
	MCPBA, $CHCl_3$, 6 d, 25°		(75)	898
	MCPBA, $CHCl_3$, 9 d, 25°		(64)	898
	PBA, benzene, 8 d, 25°		(58)	902
	TFPAA (85%), Na_2HPO_4, CH_2Cl_2, 15 min, 0°	 (77) +  (23)		904

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

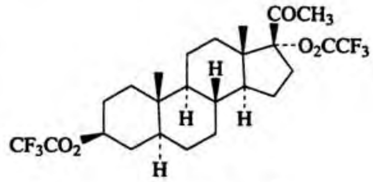
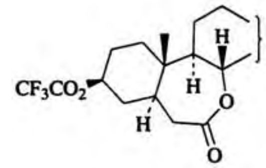
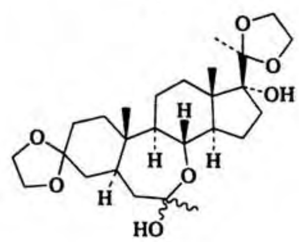
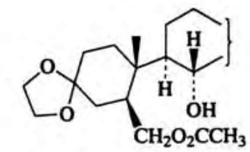
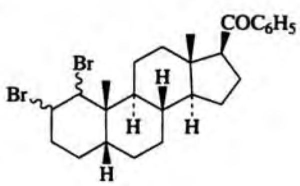
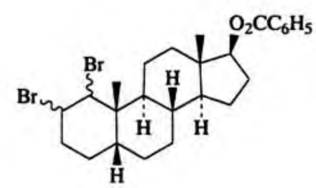
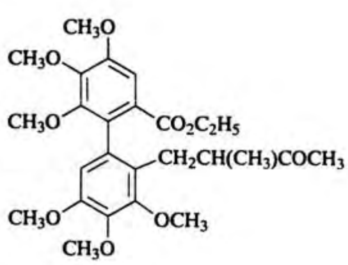
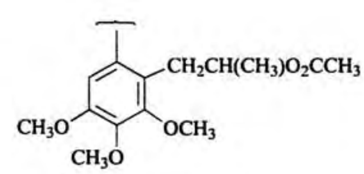
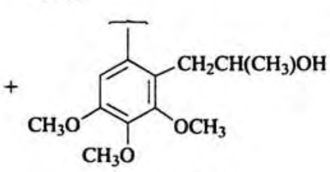
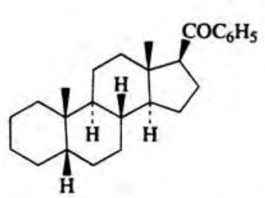
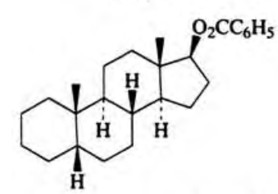
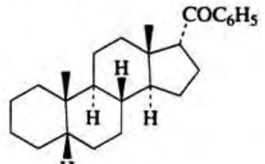
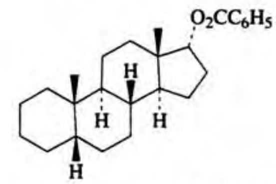
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{25}			
	87% MCPBA, $CHCl_3$, 64 h, 25°	 (70)	279
	MPPA, ether–$CHCl_3$, 1.5 h, 25°	 (>17)	279
C_{26}			
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 11 d, 25°	 (—)	905
	MCPBA, H_2SO_4, CH_2Cl_2, 5 h, 25°	 (35) +  (18) (12)*	320
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 11 d, 25°	 (—)	905
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 11 d, 25°	 (—)	905
$CH_3CO(CH_2)_2CH[(CH_2)_2OTBDPS]C_3H_7$-*i*	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, reflux	$CH_3CO_2(CH_2)_2CH[(CH_2)_2OTBDPS]C_3H_7$-*i* (60) (33)*	53

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

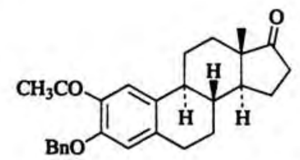
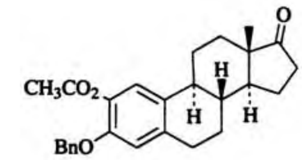
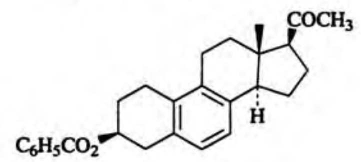
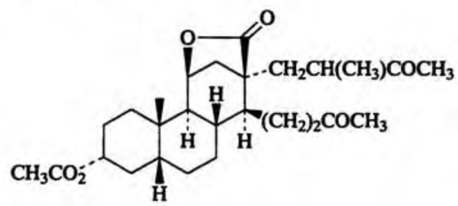
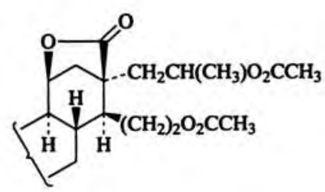
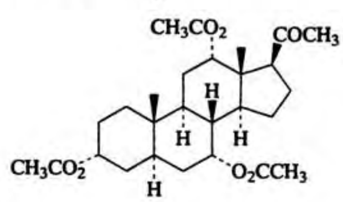
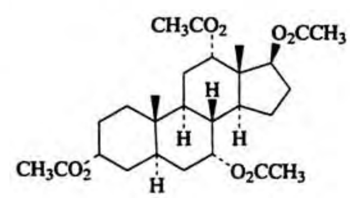
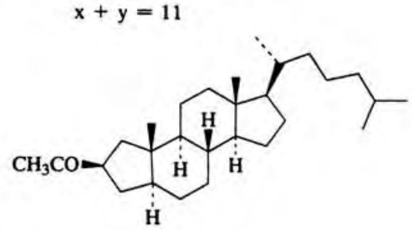
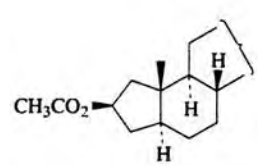
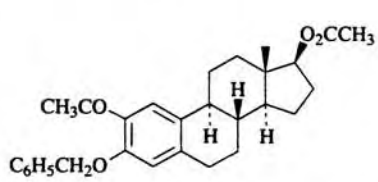
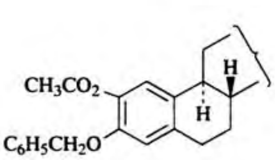
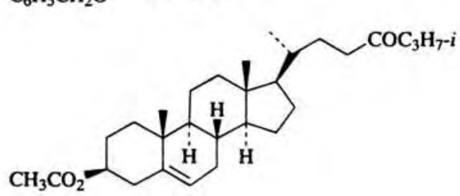
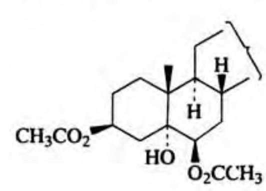
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{27}				
	PBA, $CHCl_3$, 7 d, 25°		(75)	118
	MPPA, PBA, or MCPBA		(0)	906
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1.5 h, 25° 2. 3.5 h, reflux		(79)	907
	TFPAA (90%), K_2HPO_4, CH_2Cl_2, 1 h, heat		(64)	889
C_{28}				
$CH_3(CH_2)_xCO(CH_2)_yCH_2$(p-$C_6H_5COC_6H_4CO_2$) x + y = 11	TFPAA, $CHCl_3$	Mixtures of chain insertion products	(—)	77
	MCPBA, 7 d, 0–5°		(77)	908
C_{29}				
	MCPBA, $CHCl_3$, 10 d, 25°		(65)	118
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, 25°		(—)	104

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TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

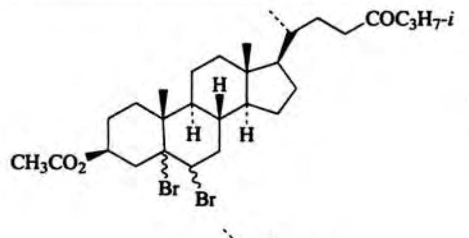
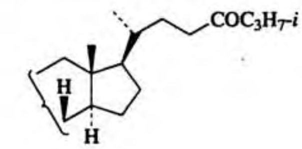
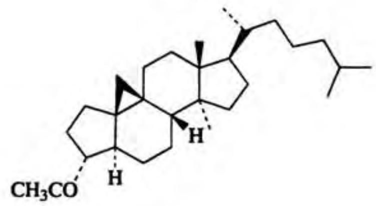
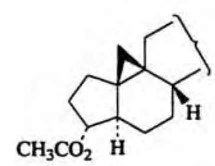
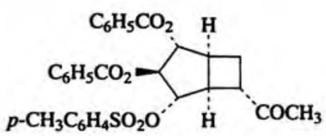
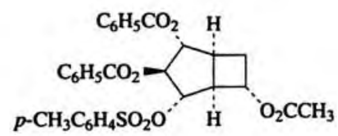
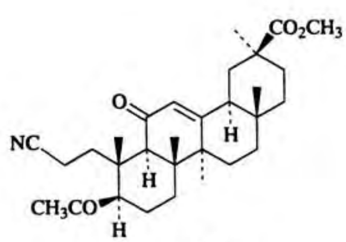
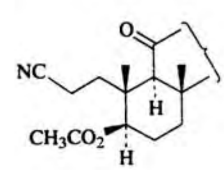
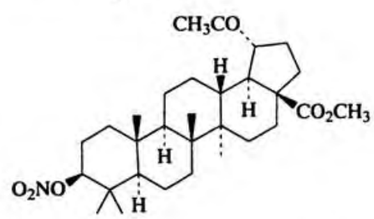
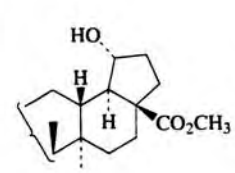
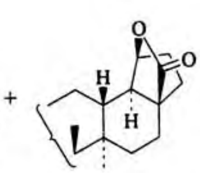
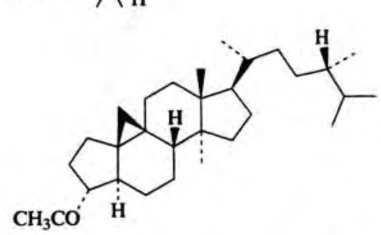
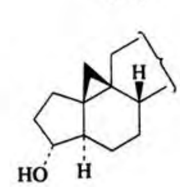
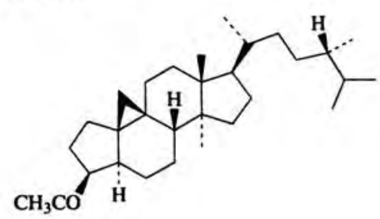
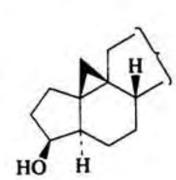
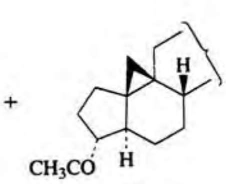
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 80 min, 25°		(100)	104
	MCPBA, CH_2Cl_2, 36 h, 20°		(34)	909, 910
C_{30}				
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 15 h, 20°		(85)	911
$CH_3(CH_2)_xCO(CH_2)_yCH_2$ — p-$C_6H_5COC_6H_4CO_2$, x + y = 13	TFPAA, $CHCl_3$	Mixtures of chain insertion products	(—)	77
	MCPBA, TsOH, CH_2Cl_2, 9 d, 25°		(57)	108
	TFPAA (90%), CH_2Cl_2, 3 d, 0°	 (18) +  (23)	(3)*	63
	TFPAA, K_2HPO_4, CH_2Cl_2, 5 h, heat		(80)	912
	1. MCPBA, ether, 60 d, 27° 2. KOH, C_2H_5OH	 (20) +  (66)		912

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TABLE I. Reactions of Straight-Chain Ketones (*Continued*)

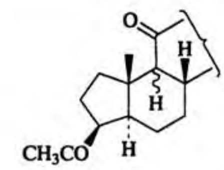
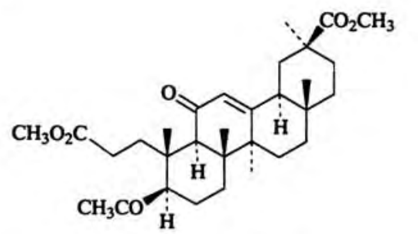
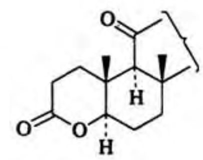
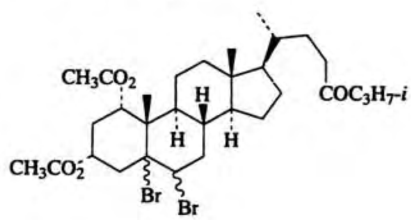
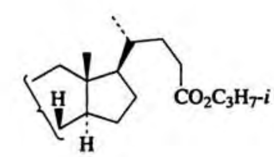
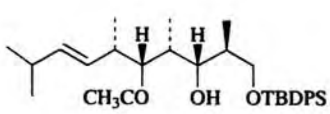
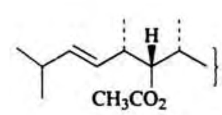
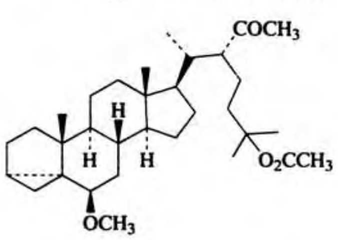
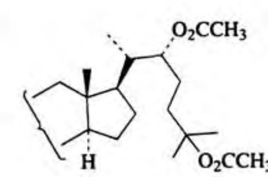
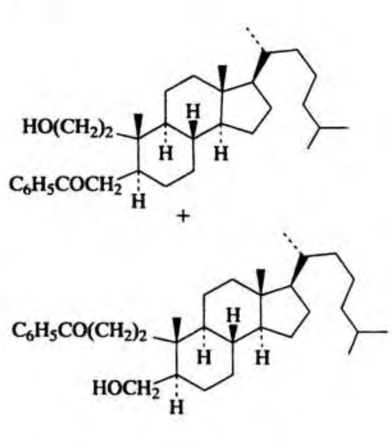
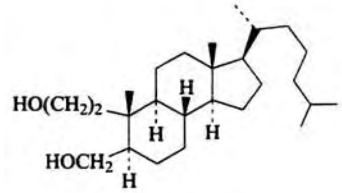
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, K_2HPO_4, CH_2Cl_2, 5 h, heat		(100)	912
C_{31}				
	MCPBA, $CHCl_3$, 6 h, heat		(—) (28)*	108
	TFPAA, Na_2HPO_4, CH_2Cl_2, 90 min, 25°		(100)	104
C_{32}				
$CH_3(CH_2)_xCO(CH_2)_yCH_2$ p-$C_6H_5COC_6H_4CO_2$ x + y = 15	TFPAA, $CHCl_3$	Mixtures of chain insertion products	(—)	77
	H_2O_2, AcOH–THF		(>87)	717
	MCPBA, $NaHCO_3$, $CHCl_3$, 25°		(34)	913
C_{33}				
	85% MCPBA, $CHCl_3$, 46 h, 25°		(>20)	914

TABLE I. REACTIONS OF STRAIGHT-CHAIN KETONES (*Continued*)

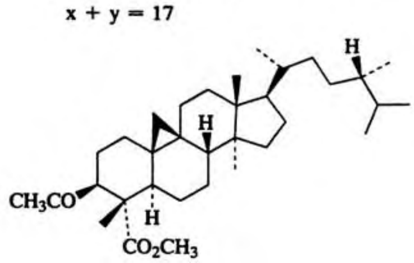
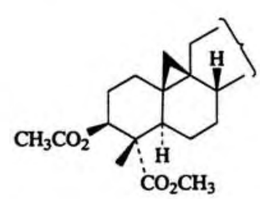
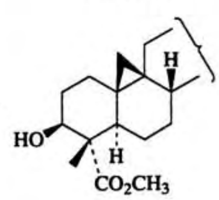
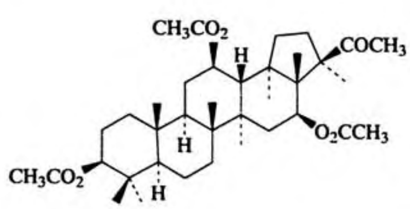
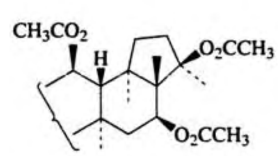
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{34}				
$CH_3(CH_2)_xCO(CH_2)_yCH_2$ / p-$C_6H_5COC_6H_4CO_2$ / $x + y = 17$	TFPAA, CH_2Cl_2	Mixtures of chain insertion products	(—)	77
	95% H_2O_2, BF_3 etherate, ether, 4 h, 25°		(41)	51
		+ 	(32)	
	HCO_3H, PAA, TFPAA, or PMA		(0)	51
C_{36}				
	PBA, $CHCl_3$		(poor)	915

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES

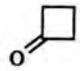
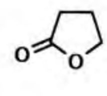
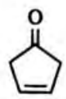
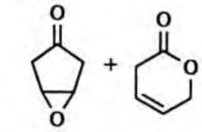
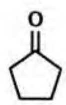
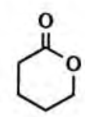
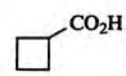
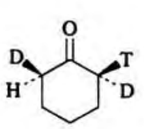
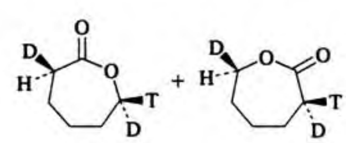
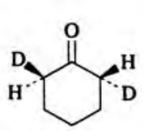
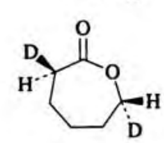
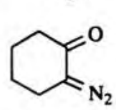
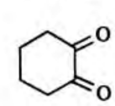
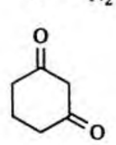
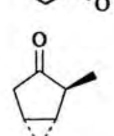
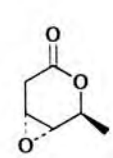
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4				
	30% H_2O_2, CF_3CH_2OH, 24 h, 25°		(98)	756, 43, 916, 917, 182, 147
C_5				
	MCPBA, CH_2Cl_2, 48 h, 20°	 I (63) + II (6)		221
	1. $[(CH_3)_3Si]_2O_2$, $(CH_3)_3SiOS(O)_2CF_3$, CH_2Cl_2, 30 h, −78° to −50° 2. 20 h, 0°	II	(42)	221
	30% H_2O_2, polystyrene–SeO_2H, 72 h		(98)	43, 220, 221, 758, 762
	20–28% PAA, acetone or $CH_3CO_2C_2H_5$, 8 h, 40°	"	(84)	754, 760
	TFPAA, TFAA, 40 min, 10–15°	"	(88)	182, 574, 742, 749, 761, 763, 918
	H_2O_2, SeO_2		(23)	920
	CAN, CH_3CN–H_2O, 4 h, 60°	$HO_2C(CH_2)_4ONO_2$ I + $HO_2C(CH_2)_2CH(CH_3)ONO_2$ II + $HO_2C(CH_2)_3ONO_2$ III + $HO_2CCH_2CH(CH_3)ONO_2$ IV; I:II:III:IV = 24:16:34:26	(50)	686
C_6				
	TFPAA (90%), Na_2HPO_4, 1.5 h, 0–25°		(>75–80)	143
	MCPBA, $CHCl_3$, 12 h, 25°		(52)	921,922
	99% MCPBA, CH_2Cl_2, 25°		(99)	218
	30% H_2O_2, H_2O, 5 d, 25–30°	$HO_2C(CH_2)_3CO_2H$	(50)	203
	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°		(98)	128

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

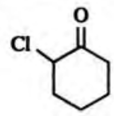
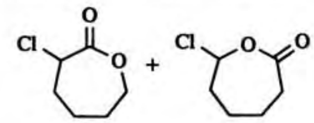
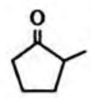
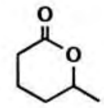
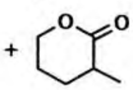
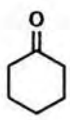
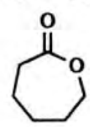
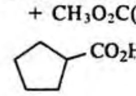
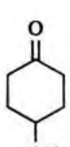
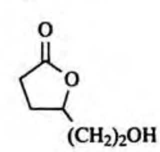
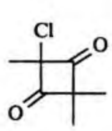
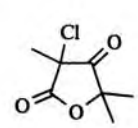
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, reflux	 (62) (6)		201
	90% H_2O_2, polystyrene–AsO_3H_2, dioxane, 25 h, 80°	$HO_2C(CH_2)_4CO_2H$	(—)	182
	MCPBA, CH_2Cl_2, 12 h, 25°	 I	(74)	134, 182, 749, 762, 763
	30% H_2O_2, Nafion, CH_2Cl_2, 36 h, heat	I +  II I:II = 85:15	(86)	220, 323
	30% H_2O_2, polystyrene–SeO_2H, 103 h	I:II = 50:50	(86)	43
	Na_2CO_4, CF_3CO_2H, 0°, 1.5 h	I:II = 72:28	(78)	763a
	35% H_2O_2, TECTA, 25°		(100)	230, 923, 924
	25% PAA, acetone, 6.25 h, 40°	"	(85)	4, 181, 182, 220, 221, 574, 748, 754, 760, 761, 762, 763, 763a, 765, 918, 919
	MCPBA (85%), CF_3CO_2H, CH_2Cl_2, 1 h, 0–25°	"	(88)	742, 921, 925
	$NaBO_3$, TFAA, 4–8 h, 50–60°	"	(79)	114
	30% H_2O_2, polystyrene–SeO_2H, 96 h	$HO_2C(CH_2)_5OH$	(71)	43
	CAN, CH_3CN–H_2O, 1 h, 60°	$CH_3O_2C(CH_2)_5ONO_2$ + $CH_3O_2C(CH_2)_3CH(CH_3)ONO_2$	(26) (17)	686
	H_2O_2, SeO_2		(32)	920
	MCPBA, CH_2Cl_2, 24 h, heat		(85)	926
C_7				
	PAA, $CHCl_3$, 25°		(70)	153

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

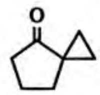
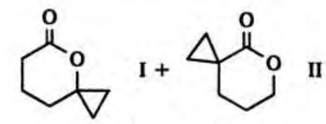
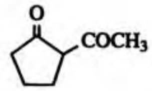
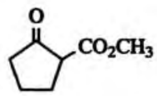
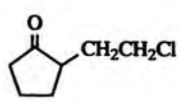
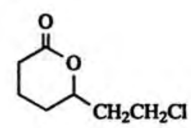
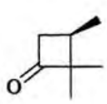
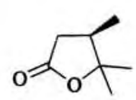
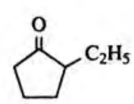
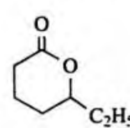
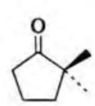
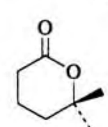
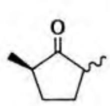
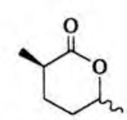
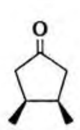
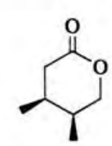
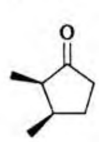
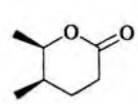
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PMA (90%), CH_2Cl_2, 24 h, reflux	 I:II = 89:11	(44)	185
	30% H_2O_2, *t*-BuOH, 16 h, heat	$HO_2CCH(CH_3)(CH_2)_3CO_2H$ I	(93)	78
	28% H_2O_2, AcOH, 12 h, 20°	I (67) + $HO_2C(CH_2)_3CO_2H$ II (7) + $HO_2CCH(CH_3)(CH_2)_2CO_2H$ III (11)		202
	28% H_2O_2, NaOH, 1 h, 20–25°	II	(58)	204
	30% H_2O_2, NaOH, 90 min, 100°	II	(74)	204
	MCPBA, CH_2Cl_2, 4–18 h, 0–25°		(80)	165
	CrO_3		(—)	693
	$K_2S_2O_8$, H_2SO_4, 12 h, 25°		(40)	158, 749
	TFPAA (85%), K_2CO_3, 12 h, 0°		(99)	164
	—		(—)	927
	MCPBA, CH_2Cl_2, 6 h, 25°		(81)	132
	TFPAA (94%), Na_2HPO_4, CH_2Cl_2, 7 h, 25°		(42)	928

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

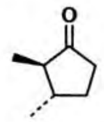
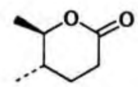
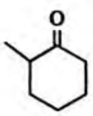
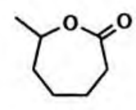
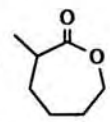
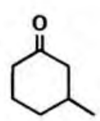
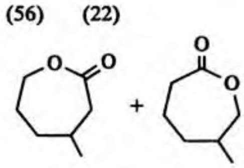
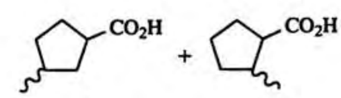
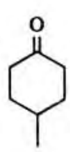
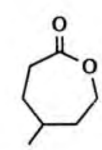
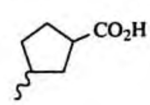
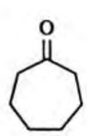
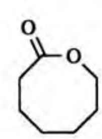
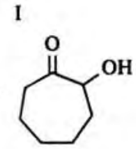
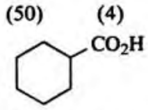
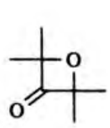
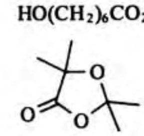
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (94%), Na_2HPO_4, CH_2Cl_2, 7 h, 25°	 (51)	928
	PAA (anh), AcOH, 8.5 h, 40°	 I (92)	138, 182, 222, 754, 762, 763
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 4 h, 25°	I +  (56) (22)	220
	20–25% PAA, AcOH, 11 h, 40°	 (81)	754
	34% H_2O_2, SeO_2, *t*-BuOH, 7 h, 80°	 I II; I:II = 85:15 (28)	680
	20–25% PAA, AcOH, 9.5 h, 40°	 (84)	754
	34% H_2O_2, SeO_2, *t*-BuOH, 7 h, 80°	 (28)	680
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2 3 h, 0° 2. 3 h, 20°	 I (68)	182 754, 919, 929
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 4 h, 25°	I +  II (50) (4)	220
	H_2O_2, SeO_2	 (34)	920
	K_2SO_5, H_2SO_4, H_2O, C_2H_5OH, 8 h, 15°	$HO(CH_2)_6CO_2C_2H_5$ (85)	930
	PAA	 (—)	931

TABLE II. Reactions of Monocyclic and Spirocyclic Ketones (*Continued*)

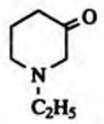
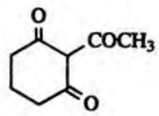
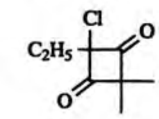
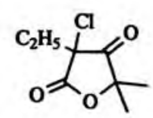
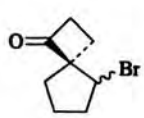
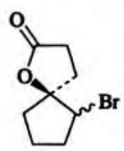
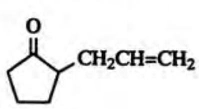
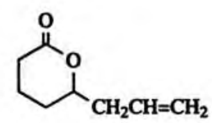
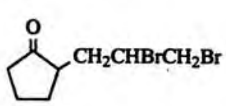
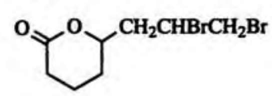
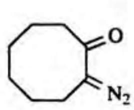
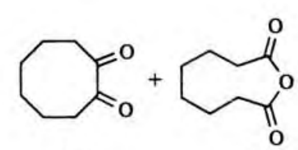
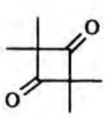
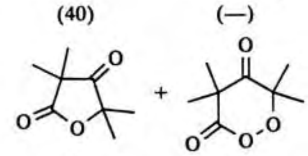
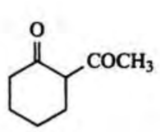
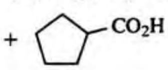
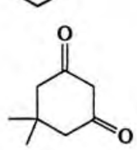
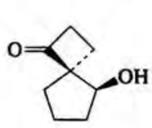
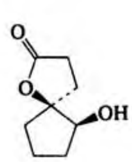
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, C_2H_5OH, 1–14 d	$C_2H_5NH(CH_2)_3CO_2H$	(76)	73
	28% H_2O_2, 20°	$HO_2C(CH_2)_3CO_2H$	(76)	203
	PAA, $CHCl_3$, 25°		(55)	153
	MCPBA		(84)	194
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°		(>55)	130
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 3 h, 25°	"	(64)	220
	$K_2S_2O_8$, H_2SO_4, H_2O		(>16)	159
	99% MCPBA, CH_2Cl_2, 25°	 (40) (—)		218
	98% H_2O_2, CH_3CN, 11 d, 25°	 I (85–90) II (9)		932, 933
	TFPAA, $CHCl_3$	I	(77)	934
	30% H_2O_2, *t*-BuOH, 3 h, heat	$HO_2C(CH_2)_4CH(CH_3)CO_2H$	(1–2)	204, 78
		+ 	(87)	
	30% H_2O_2, H_2O, 5 d, 25–30°	$HO_2CCH_2C(CH_3)_2CH_2CO_2H$	(47)	203
	—		(—)	194

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

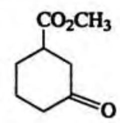
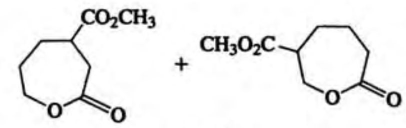
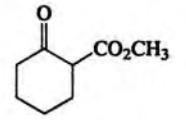
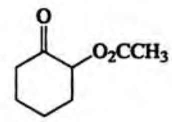
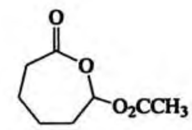
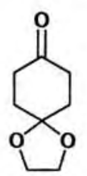
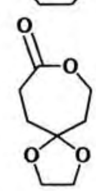
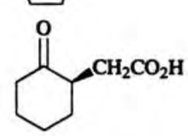
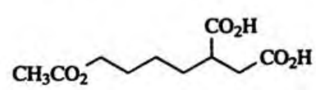
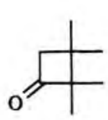
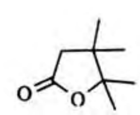
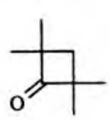
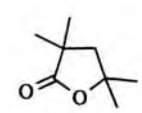
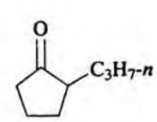
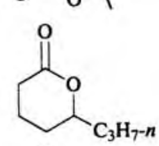
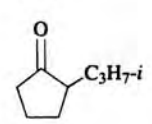
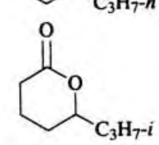
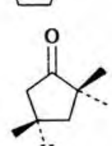
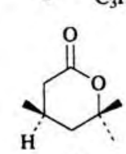
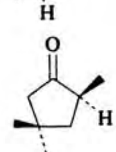
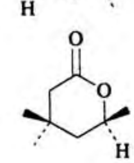
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	24% PAA, $CH_3CO_2C_2H_5$, 18 h, 65–70°	 no ratio	(50)	205
	90% H_2O_2, polystyrene–AsO_3H_2, 26 h, 80°		(0)	182
	MCPBA, $CHCl_3$, 2.5 h, 25°		(86)	199
	TFPAA, Na_2HPO_4, CH_2Cl_2		(89)	935
	H_2O_2, AcOH, 3 h, 70°		(62)	37
	H_2O_2, KOH		(—)	150
	$K_2Cr_2O_7$, H_2SO_4, H_2O, 20 h, 45°		(53) + (5)*	694, 695
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, 25°		(41)	158, 159, 749
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°		(37)	158
	40% PAA, NaOAc, $CHCl_3$, 18 h, 25°		(79)	155
	40% PAA, NaOAc, $CHCl_3$, 18 h, 25°		(84)	155

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

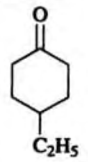
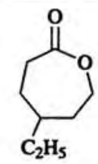
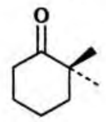
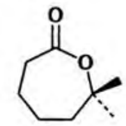
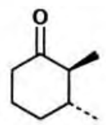
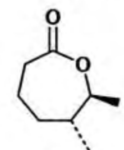
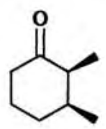
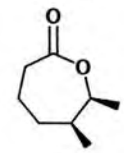
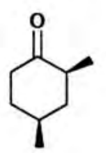
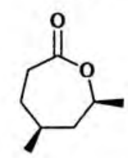
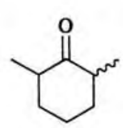
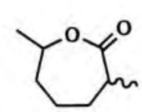
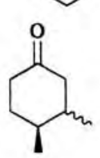
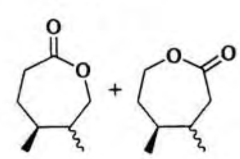
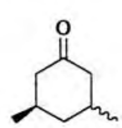
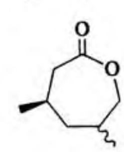
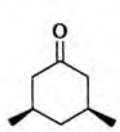
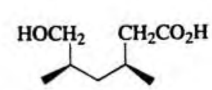
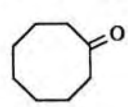
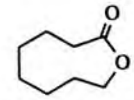
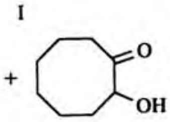
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	40% PAA, 65° then 1.5 h, 25°		(71)	936
	MCPBA, NaOAc, CH_2Cl_2, heat		(—)	168
	MCPBA, CH_2Cl_2, 2 h, reflux		(80)	140
	MCPBA, CH_2Cl_2, 2 h, reflux		(80)	140
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2.5 h, 25°		(94)	167
	30% H_2O_2, polystyrene–SeO_2H, 108 h		(92)	43, 754
	PAA, AcOH, 6.75 h, 50°		(85)	754
	PAA, AcOH, 8.75 h, 50°		(92)	754
	—		(—)	142
	PMA (90%), CH_2Cl_2, 0°	 I	(80)	44, 919, 929, 937
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 4 h, 25°	I +  II (11) (42)		220
	21% PAA, $CH_3CO_2C_2H_5$, 8.5 h, 70°	I + $HO_2C(CH_2)_6CO_2H$ (6) (59)		754

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

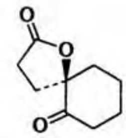
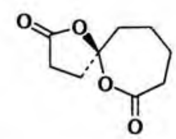
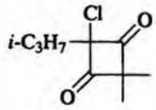
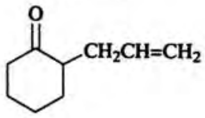
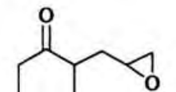
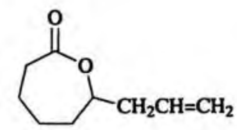
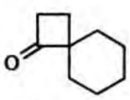
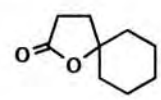
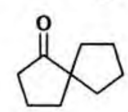
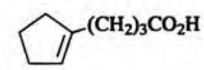
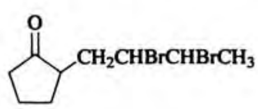
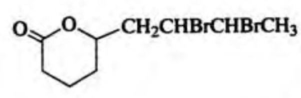
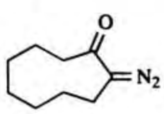
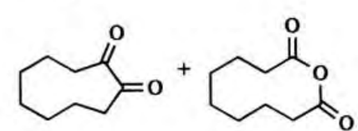
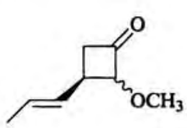
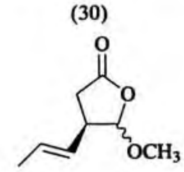
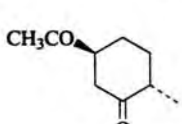
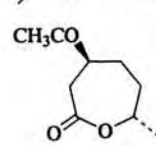
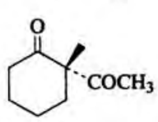
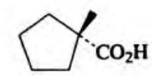
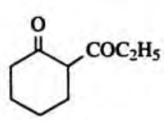
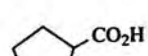
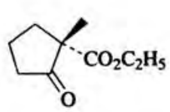
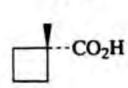
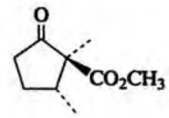
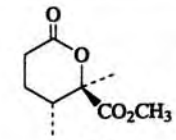
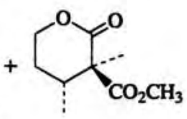
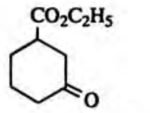
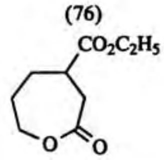
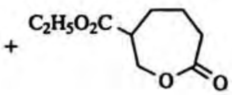
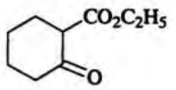
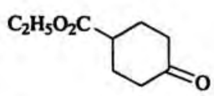
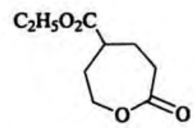
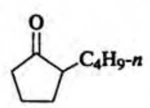
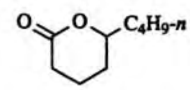
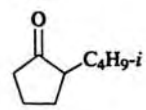
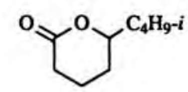
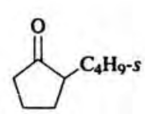
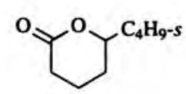
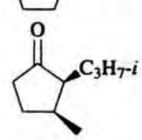
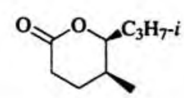
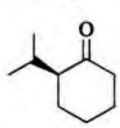
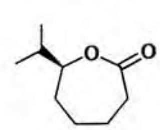
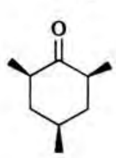
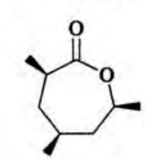
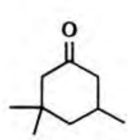
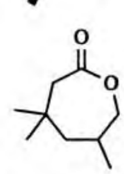
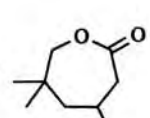
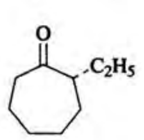
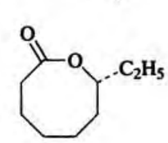
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	MCPBA, CH_2Cl_2, 1 h, 20°	 (85)	200
	PAA, $CHCl_3$, 25°	No reaction (0)	153
	50% H_2O_2, C_6H_5CN, $KHCO_3$, CH_3OH, 40 h, 25°	 (54)	184
	42% PAA, $CHCl_3$, 48 h, 0°	 I (44)	182, 184, 221
	BPC, THF, 1 h, 0–25°	I (70)	102, 182, 184, 221
	30% H_2O_2, NaOH, CH_3OH, 2 h, 25°	 (83)	148, 190, 192, 193
	MCPBA, $ClCH_2CH_2Cl$, 6 h, heat	 (>81)	938
	K_2SO_5, H_2SO_4, H_2O, 12 h, <10°	 (19)	159
	99% MCPBA, CH_2Cl_2, 25°	 (30) + (—)	218
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 (78)	198a
	MCPBA, CH_2Cl_2, 25°	 (79)	110
	28% H_2O_2, H_2O, 12 h, 20°	 (90) + $HO_2C(CH_2)_4CO_2H$ (4) + $HO_2CC(CH_3)_2(CH_2)_4CO_2H$ (trace)	78, 202
	30% H_2O_2, NaOH, 1 h, 20–25°	 (59) + $HO_2C(CH_2)_4CO_2H$ (4)	204
	1. 98% H_2O_2, H_2SO_4 2. benzene, 6 h, heat	 (64)	774

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, Li_2CO_3, CH_2Cl_2, 13.5 h, reflux	 (76) +  (13)	145, 206
	24% PAA, $CH_3CO_2C_2H_5$, 6 h, 70°	 +  (93)	205
	24% PAA, $CH_3CO_2C_2H_5$, 60–70°	$C_2H_5O_2CCO(CH_2)_4CO_2H$ (80)	205
	24% PAA, $CH_3CO_2C_2H_5$, 18 h, 60°	 (55)	205
	K_2SO_5, H_2SO_4, H_2O, 12 h, 25°	 (57)	158, 159, 749
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°	 (33)	158
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°	 (50)	158
	MCPBA, $NaHCO_3$, CH_2Cl_2, 3 d, 25°	 (64)	FKPs
	PAA, AcOH, 9 h, 50°	 (85)	754
	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 4 h, 25°	 (98)	141, 167
	PAA, AcOH, 13 h, 50°	 +  (70)	754
	TFPAA (>85%), NaH_2PO_4, CH_2Cl_2, 0–25°	 (70)	174

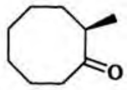
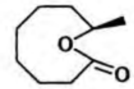
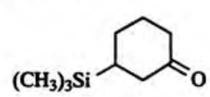
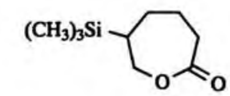
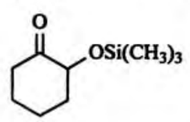
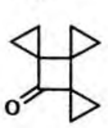
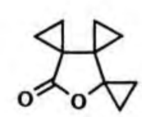
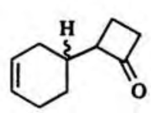
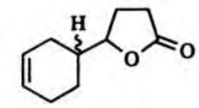
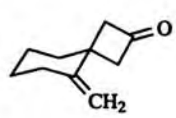
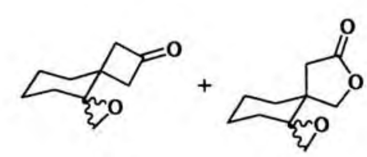
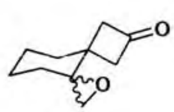
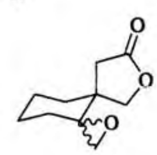
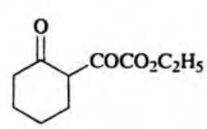
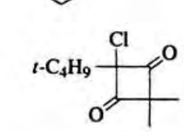
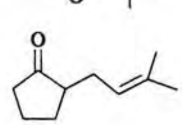
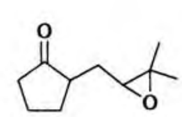
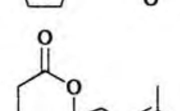
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2	 (>52)	939
	MCPBA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 (99)	94
	MCPBA, ether, 18 h, 25°	$CH_3O_2C(CH_2)_4CH(OCH_3)_2$ I + $CH_3O_2C(CH_2)_4CO_2CH_3$ II I:II = 36:64 (90)	197
	H_2O_2, AcOH, H_2SO_4	 (—)	940
	30% H_2O_2, NaOH, CH_3OH, 2.5 h, 25°	 (82)	148, 190, 192
C_{10}			
	MCPBA (1 eq), $CHCl_3$, 6 d, 25°	 I (71) + II trace	219
	MCPBA (3 eq), $CHCl_3$, 6 d, 25°	II (77)	219
	MCPBA, $CHCl_3$, 6 d, 25°	 (74)	219
	30% H_2O_2, KOH, 1 h, 20–25°	$HO_2CCO_2C_2H_5$ (50) + $HO_2C(CH_2)_5CO_2H$ (3)	203
	PAA, $CHCl_3$, 25°	(0)	153
	MCPBA, CH_2Cl_2	 (89)	220
	$[(CH_3)_3Si]_2O_2$, BF_3 etherate, CH_2Cl_2, 4.5 h, 25°	 (44)	220

TABLE II. Reactions of Monocyclic and Spirocyclic Ketones (*Continued*)

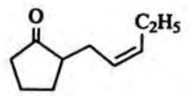
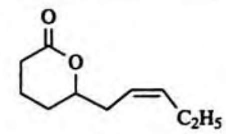
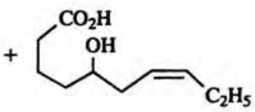
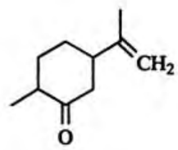
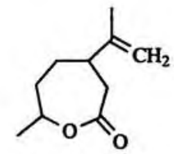
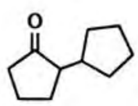
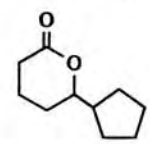
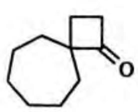
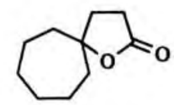
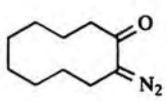
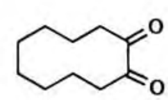
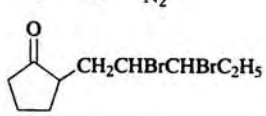
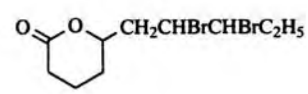
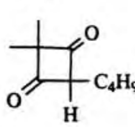
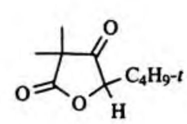
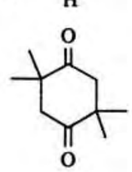
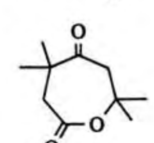
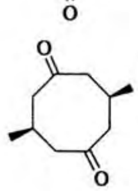
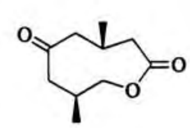
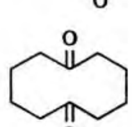
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$[(CH_3)_3Si]_2O_2$, BF_3 etherate, CH_2Cl_2, 4.5 h, 25°	 (50) +  (8)	220
	40% PAA	 (—)	682
	MCPBA, $CHCl_3$, 25°	 (—)	697
	30% H_2O_2, NaOH, CH_3OH–H_2O	 (100)	148, 190, 192
	99% MCPBA, CH_2Cl_2, 25°	 (95)	218
	PBA, TsOH, $CHCl_3$, 4 h, 0–25°	 (>67)	156, 159
	PAA, $CHCl_3$, 25°	 (15)	153
	MCPBA, CH_2Cl_2, 20°	 (75)	172
	TFPAA, Na_2HPO_4, 2 h, 0°, 1 h, 25°	 (82)	211
	MCPBA, CH_2Cl_2, 31 d, 25°, or 48 h, 45°	(0)	196

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

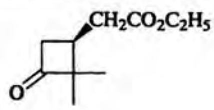
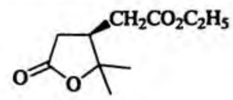
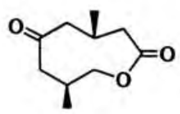
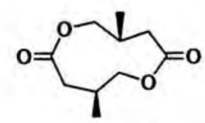
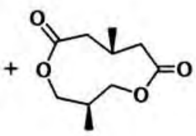
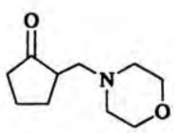
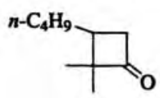
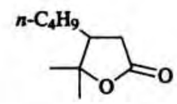
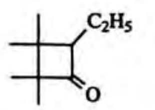
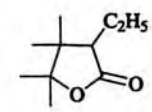
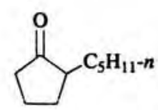
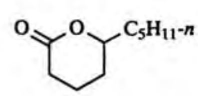
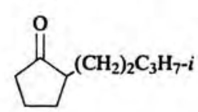
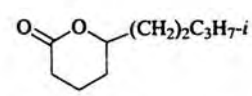
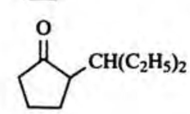
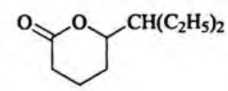
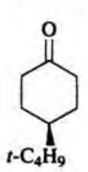
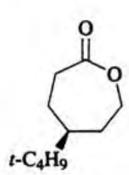
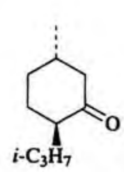
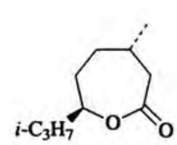
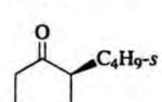
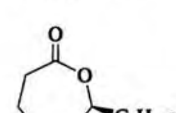
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, $CHCl_3$, 15d	 (—)	692
	TFPAA, Na_2HPO_4, 2 h, 0°, 48 h, 25°	 (12) +  (3)	211
	15% H_2O_2, NaOH, C_2H_5OH, −10 to 25°	$CH_3CO(CH_2)_3CO_2H$ (33)	158
	30% H_2O_2, NaOH, CH_3OH, 4 h, 25°	 (64)	152
	30% H_2O_2, NaOH, CH_3OH, 4 h, 25°	 (95)	152
	K_2SO_5, H_2SO_4, 4 h, 25°	 (51)	158, 159, 749
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°	 (38)	158
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°	 (43)	158
	$[(CH_3)_3Si]_2O_2$, BF_3 etherate, CH_2Cl_2, 2 d, 25°	 (88)	220, 221, 222, 941
	MCPBA (2 eq), solid state, 30 min, 25°	" (95)	740
	MCPBA, $CHCl_3$	" (94)	740
	MCPBA	 (80)	183, 492, 942
	PAA, AcOH, 13 h, 50°	 (92)	754

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

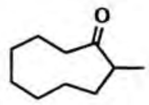
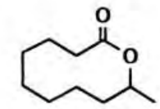
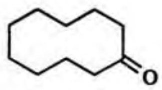
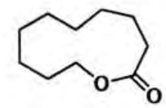
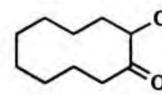
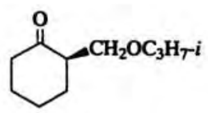
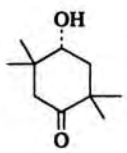
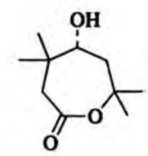
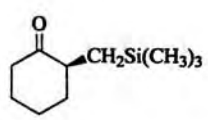
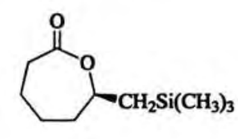
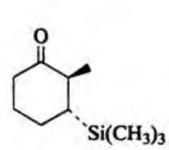
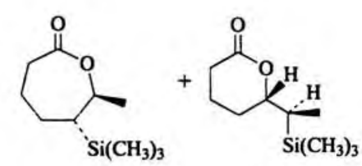
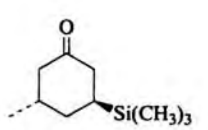
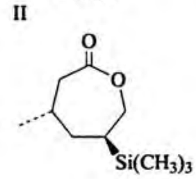
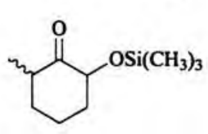
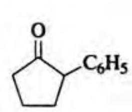
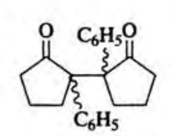
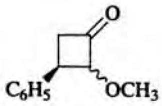
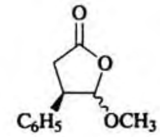
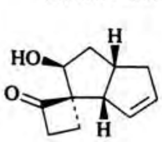
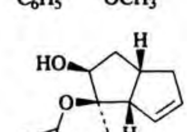
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, TBMP, 50°		(61)	131
	MCPBA, $CHCl_3$, 48 h, heat	 I	(87)	177, 178
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 3 h, 25°	I (24) +  (35)		220
	28% H_2O_2, Na_2CO_3, 1 h, 25°	$HO_2C(CH_2)_4CO_2H$	(70)	204
	85% MCPBA, CH_2Cl_2, 3 d, 20°		(85)	172, 943
	MCPBA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°		(96)	94
	MCPBA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 I major + II minor	(>75)	94
	MCPBA, CH_2Cl_2, 4 h, 25°	II	(>63)	94
	MCPBA, Na_2HPO_4, CH_2Cl_2–H_2O, 2.5 h, 25°		(88)	208
	MCPBA, ether, 18 h, 25°	$CH_3O_2CCH(CH_3)(CH_2)_3CH(OCH_3)_2$	(50–60)	197
C_{11} 	15% H_2O_2, NaOH, 20 min, −10 to 25°	 (24) + $C_6H_5CO(CH_2)_3CO_2H$ (33)	(41)*	179
 *cis:trans* = 9:91	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°		(81)	198a
	H_2O_2, NaOH		(—)	194

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

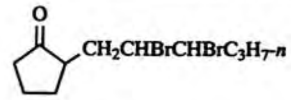
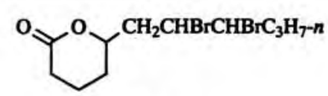
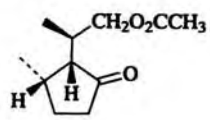
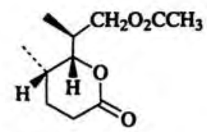
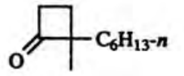
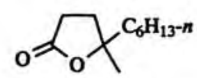
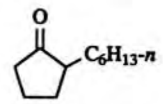
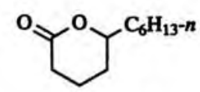
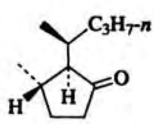
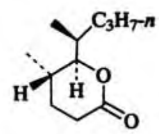
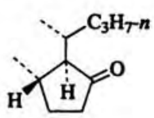
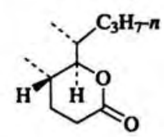
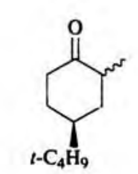
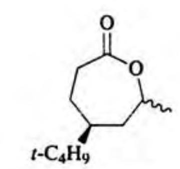
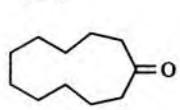
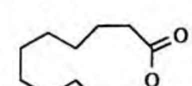
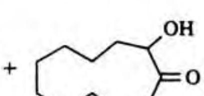
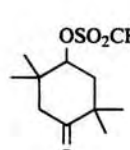
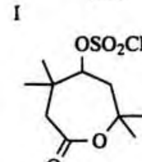
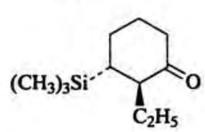
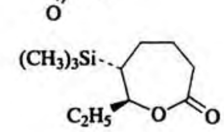
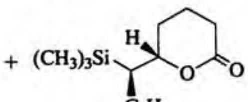
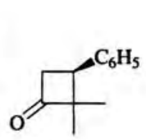
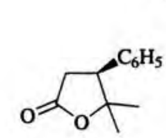
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	K_2SO_5, H_2SO_4, H_2O, 12 h, <10°		(22)	159
	MCPBA, $NaHCO_3$, CH_2Cl_2, 23 h, 5°		(73)	133
	30% H_2O_2, NaOH, CH_3OH, 2 h, 25°		(100)	148, 190, 192
	K_2SO_5, H_2SO_4, 4 h, 25°		(47)	158, 159, 749
	MCPBA, $CHCl_3$, 60°		(—)	157
	MCPBA, $CHCl_3$, 60°		(—)	157
	$C_6H_5SeO_3H$, Na_2HPO_4, CH_2Cl_2, 2 h		(83)	222
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 4 h, 25°	 +  I (30) II (33)		220
	MCPBA, $CHCl_3$, 48 h, heat	I	(87)	177, 178
	85% MCPBA, CH_2Cl_2, 4 d, 20°		(85)	173, 943
	MCPBA, CH_2Cl_2, 4 d, 25°	 + 	(94)	207
C_{12}				
	MCPBA, $NaHCO_3$		(100)	146

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

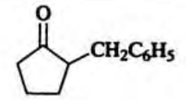
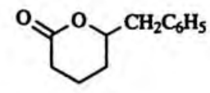
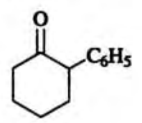
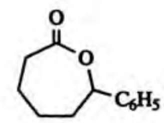
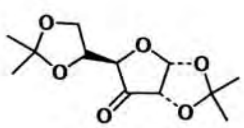
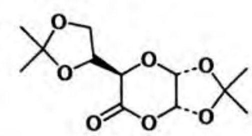
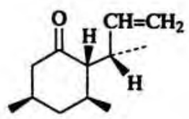
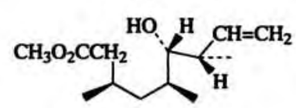
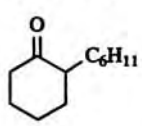
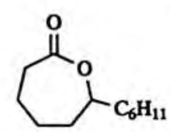
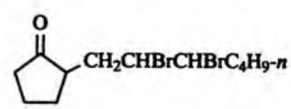
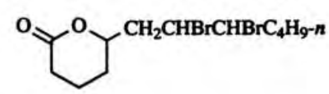
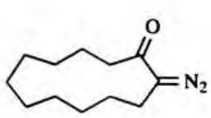
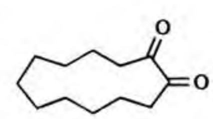
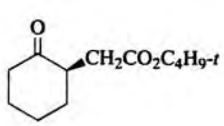
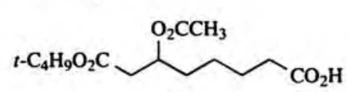
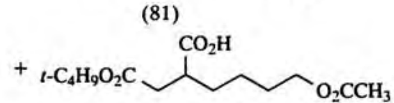
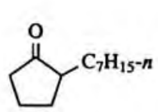
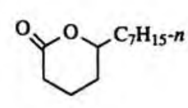
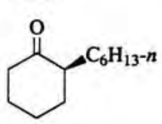
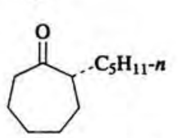
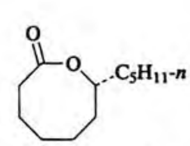
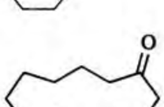
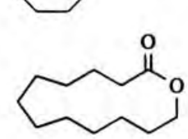
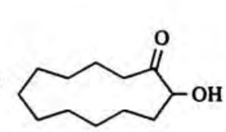
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, AcOH, acetone or $CH_3CO_2C_2H_5$, 8 h, 40°		(85)	158, 183
	90% H_2O_2, polystyrene–AsO_3H_2, dioxane, 15 h, 80°		(85)	180, 181, 182, 762
	MCPBA, $CHCl_3$, <2 h, 25°		(65)	301
	30% H_2O_2, $C_6H_5SeO_2H$, Na_2HPO_4, THF, 13 h, 45°		(63)	222
	PAA (anh), AcOH, 10 h, 50°		(82)	754
	K_2SO_5, H_2SO_4, H_2O, 12 h, <10°		(23)	159
	99% MCPBA, CH_2Cl_2, 25°		(92)	218
	H_2O_2, AcOH, 3 h, 70°	 (81) +  (trace)		37
	K_2SO_5, H_2SO_4, 4 h, 25°		(49)	158, 159, 749
	PAA	n-$C_6H_{13}CHOH(CH_2)_4CO_2H$	(74–90)	171
	TFPAA (>85%), NaH_2PO_4, CH_2Cl_2, 0–25°		(—)	174
	$[(CH_3)_3Si]_2O_2$, $SnCl_4$, CH_2Cl_2, 2.5 h, 25°	 I (62) +  II (20)		220

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

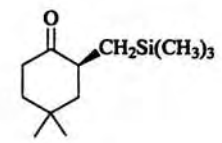
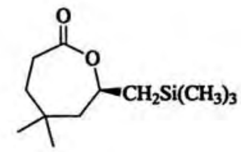
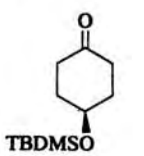
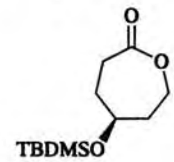
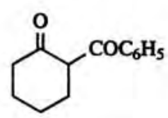
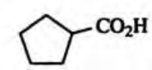
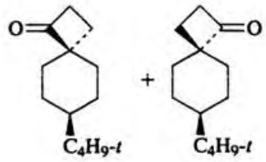
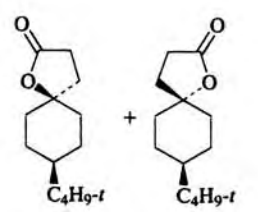
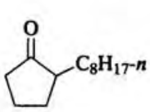
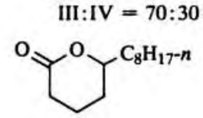
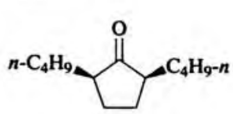
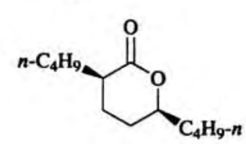
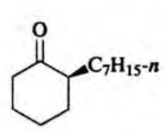
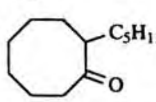
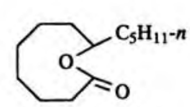
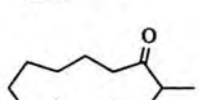
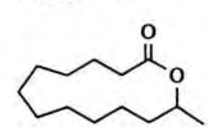
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, 20 h, heat	I	(90)	177, 178, 744, 944, 945, 946, 947, 948
	MCPBA, Na_2HPO_4, CH_2Cl_2, 3 h, 25°		(92)	139
	MCPBA, CH_2Cl_2, 24 h, heat		(67)	926
C_{13}				
	30% H_2O_2, H_2SO_4, *t*-BuOH, 2 h, 100°		(85)	78, 204
 I II I:II = 70:30	30% H_2O_2, NaOH, CH_3OH–H_2O	 III (70) IV (30) III:IV = 70:30		148, 190, 192
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°		(53)	158, 749
	30% H_2O_2, AcOH, 3 d, 50°		(30)	949
	PAA	*n*-$C_7H_{15}CHOH(CH_2)_4CO_2H$	(74–90)	171
	TFPAA, Na_2HPO_4, CH_2Cl_2		(75)	939
	MCPBA, $CHCl_3$, 70°		(91)	175, 176, 177, 178

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

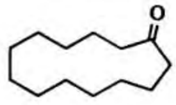
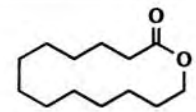
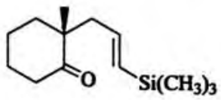
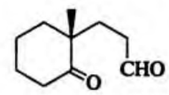
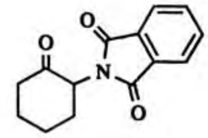
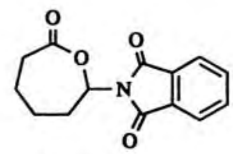
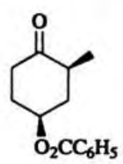
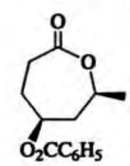
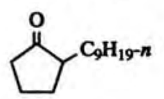
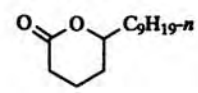
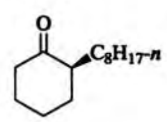
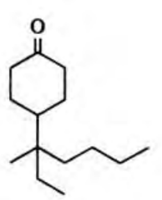
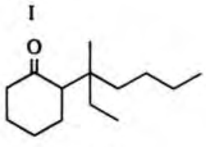
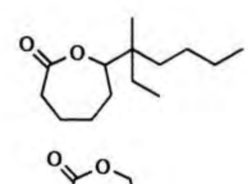
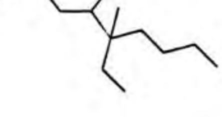
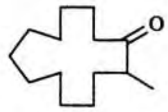
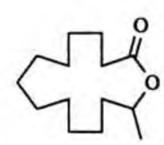
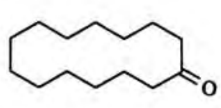
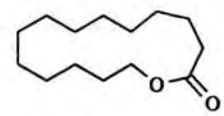
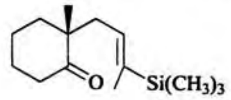
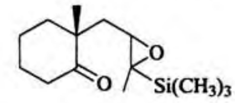
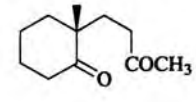
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 48 h, heat	 (87)	177, 178
	MCPBA, 29 h, 25°	 (60)	217
C_{14}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 3 h, 25°	 (43)	201
	MCPBA, $NaHCO_3$, CH_2Cl_2, 0°	 (90)	137
	$K_2S_2O_8$, H_2SO_4, H_2O, 12 h, <10°	 (37)	158
	PAA	n-$C_8H_{17}CHOH(CH_2)_4CO_2H$ (75–90)	171
 I +  II I:II = 88:12	PAA (anh), AcOH, 11 h, 50°	 +  (80)	754
	40% PAA, BF_3 etherate, $CHCl_3$, 40 h, 45°	 (65)	176
	MCPBA, $CHCl_3$, 48 h, heat	 (87)	177, 178
	MCPBA, CH_2Cl_2, 10 min, 0°	 (>90)	217
	MCPBA, CH_2Cl_2, 4 h, 25°	 (90)	217

TABLE II. Reactions of Monocyclic and Spirocyclic Ketones (*Continued*)

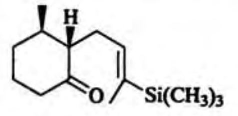
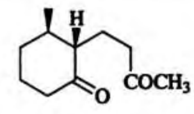
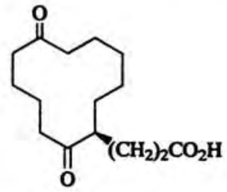
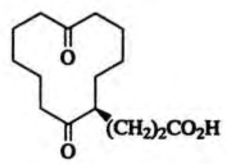
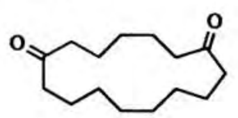
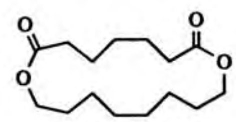
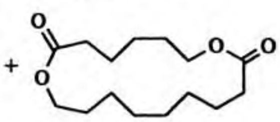
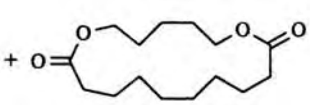
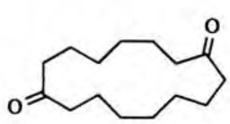
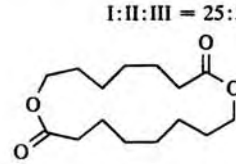
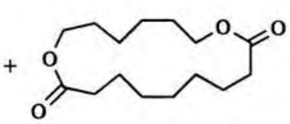
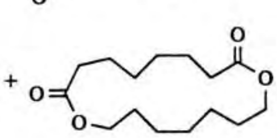
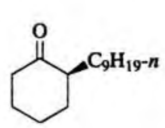
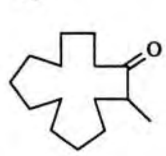
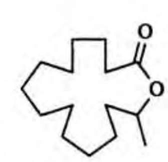
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. MCPBA, CH_2Cl_2, 4 h, 25° 2. HCO_2H		(83)	217
C_{15}				
	1. TFPAA (90%), Na_2HPO_4, 30 min, 20° 2. 1 h, heat	$HO_2C(CH_2)_4OH$ + $HO_2C(CH_2)_4CO_2H$ + $HO(CH_2)_4OH$	(71)	849
	1. TFPAA (90%), Na_2HPO_4, 30 min, 20° 2. 1 h, heat	$HO_2C(CH_2)_5CO_2H$ + $HO_2C(CH_2)_4CO_2H$	(—)	849
	1. TFPAA (90%), Na_2HPO_4, 30 min, 20° 2. 1 h, heat	 I +  II +  III I:II:III = 25:50:25	(100)	861
	TFPAA, Na_2HPO_4, 1.5 h, heat	 I +  II +  III I:II:III = 50:25:25	(96)	861
	PAA	n-$C_9H_{19}CHOH(CH_2)_4CO_2H$	(74–90)	171
	40% PAA, BF_3 etherate, $CHCl_3$, 40 h, 45°		(58)	176

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

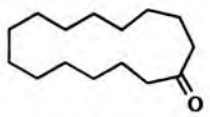
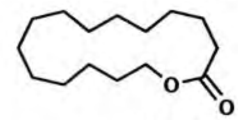
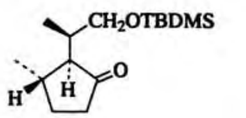
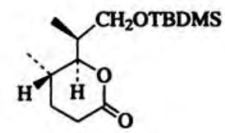
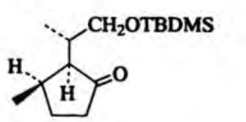
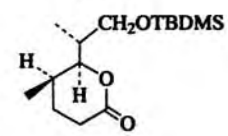
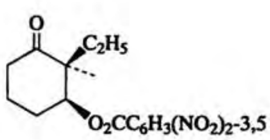
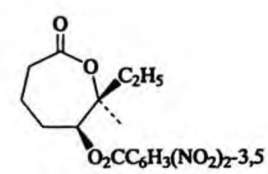
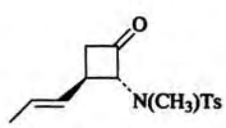
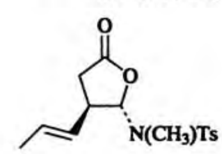
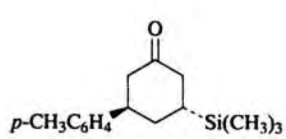
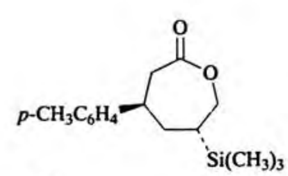
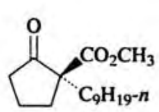
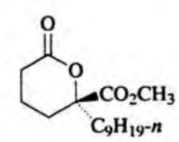
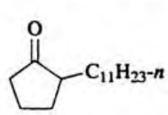
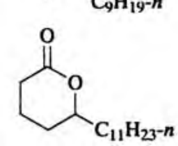
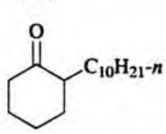
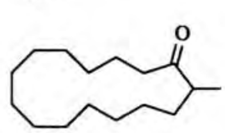
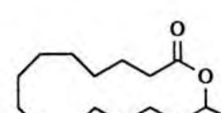
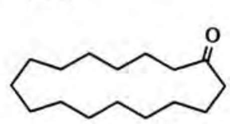
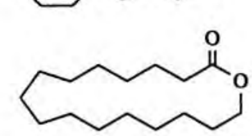
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $CHCl_3$, 48 h, heat		(87)	177, 178
	MCPBA, $NaHCO_3$, CH_2Cl_2, 0–5°		(90)	417
	MCPBA, $NaHCO_3$, CH_2Cl_2, 14 h, 5–25°		(95)	133, 416
C_{16}				
	MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°		(100)	135
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°		(84)	198a
	MCPBA, Na_2HPO_4, CH_2Cl_2–H_2O, 2.5 h, 25°		(94)	208, 209
	MCPBA, $NaHCO_3$, $CHCl_3$, 48 h, 25°		(>85)	950
	MCPBA, $CHCl_3$, 20 h, 25°		(—)	684
	PAA	n-$C_{10}H_{21}CHOH(CH_2)_4CO_2H$	(74–90)	171
	40% PAA, BF_3 etherate, $CHCl_3$, 40 h, 45°		(65)	176
	MCPBA, $CHCl_3$, 48 h, heat		(87)	177, 178, 945, 951

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

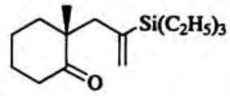
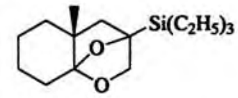
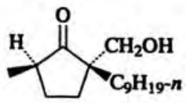
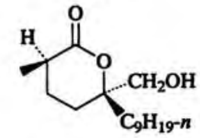
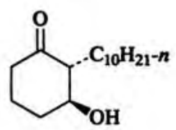
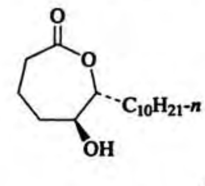
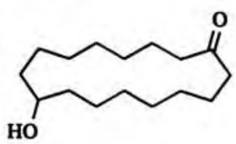
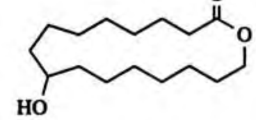
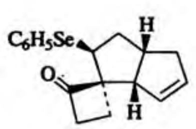
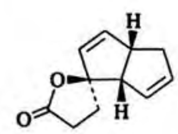
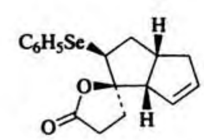
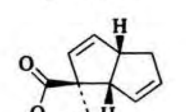
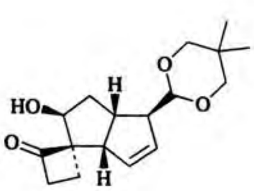
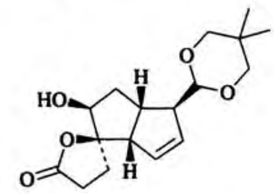
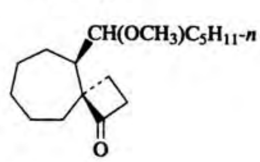
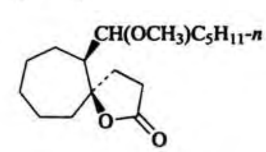
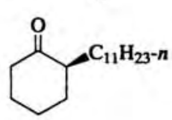
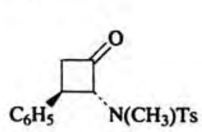
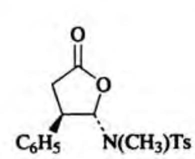
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2, 25°	 (—)	217
	MCPBA, $NaHCO_3$, $CHCl_3$, 5.5 d, 25°	 (84)	166
	MCPBA	 (>61)	170
	40% PAA, BF_3 etherate, $CHCl_3$, 12 h, 50°	 (30)	951
C_{17}			
	1. 64% MCPBA, CH_2Cl_2, 15 min, −78° 2. 15 min, 0° 3. $C_2H_5OCH{=}CH_2$, 88 h	 (65)	195, 213
	1. 30% H_2O_2, NaOH, THF–CH_3OH, 30 min 2. Na_2SO_3	 (70)	195, 212
	30% H_2O_2, C_2H_5OH, reflux	 (—)	212
	H_2O_2, NaOH, CH_3OH, −25°	 (92)	194, 195
	H_2O_2, NaOH, CH_3OH	 (93–98)	191
	PAA	n-$C_{11}H_{23}CHOH(CH_2)_4CO_2H$ (75–90)	171
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 (93)	198a

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

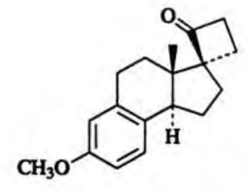
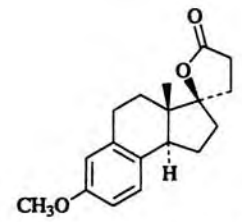
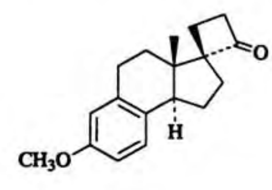
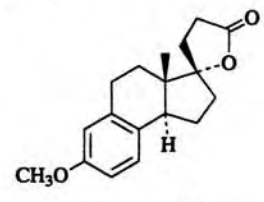
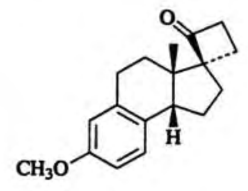
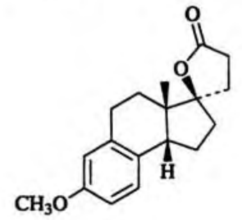
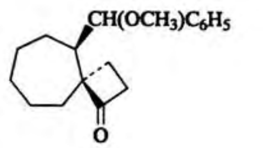
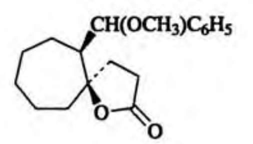
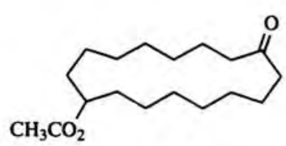
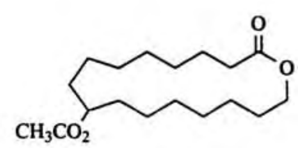
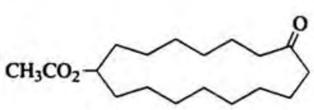
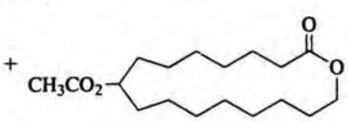
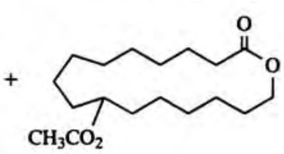
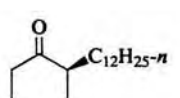
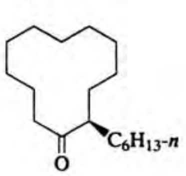
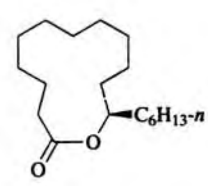
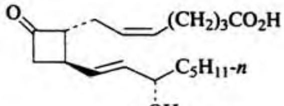
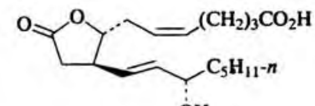
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{18}				
	70% t-BuO_2H, NaOH, THF, 1.6 h, 0°		(92)	186
	70% t-BuO_2H, NaOH, THF, 1.6 h, 0°		(85)	186
	70% t-BuO_2H, NaOH, THF, 1.6 h, 0°		(79)	186
	H_2O_2, NaOH, CH_3OH		(93–98)	191
	40% PAA, BF_3 etherate, 12 h, 50°		(44)	945
+ 		+ 		
		+ 		
	PAA	n-$C_{12}H_{25}CHOH(CH_2)_4CO_2H$	(74–90)	171
	40% PAA, BF_3 etherate, $CHCl_3$, 48 h, 45°		(49) (33)*	175
C_{19}				
	30% H_2O_2, AcOH, 12 h, 0–5°		(95)	151, 224

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

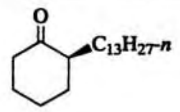
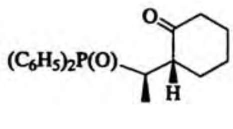
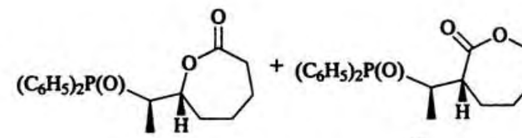
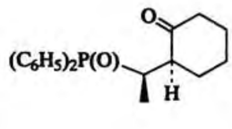
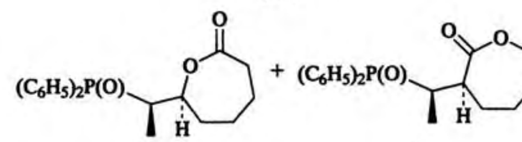
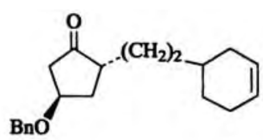
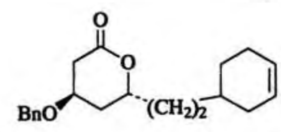
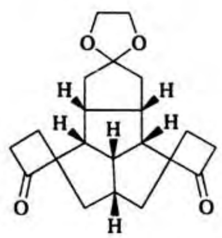
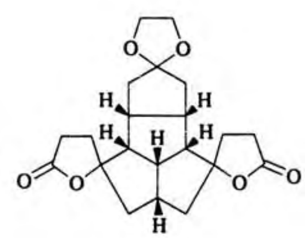
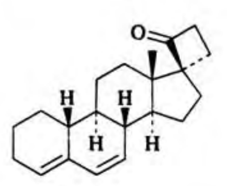
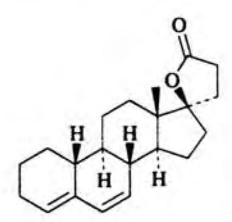
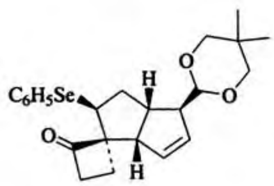
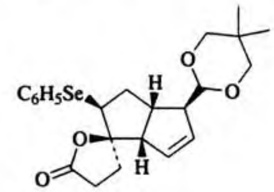
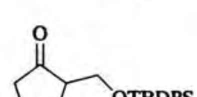
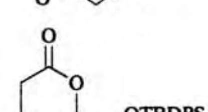
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PAA	n-$C_{13}H_{27}CHOH(CH_2)_4CO_2H$ (74–90)	171
C_{20}			
	—	 I + II; I:II = 96:4 (89)	210
	—	 I + II; I:II = 63:37 (—)	210
	1. $[(CH_3)_3Si]_2O_2$, BF_3 etherate, CH_2Cl_2, 2 h, 0° 2. 2 h, 25°	 (57–60)	163
C_{21}			
	H_2O_2, NaOH, CH_3OH	 (91)	189
	30% H_2O_2, NaOH, CH_3OH	 (—)	187
	H_2O_2, NaOH, CH_3OH–H_2O	 (77)	195
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°, 4 h	 (86)	209a

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

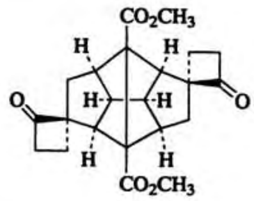
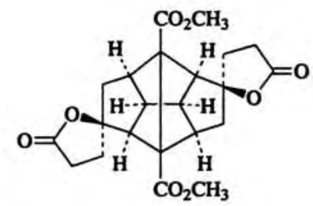
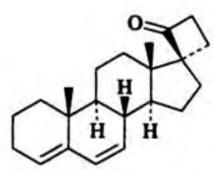
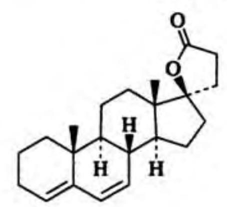
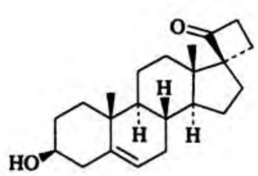
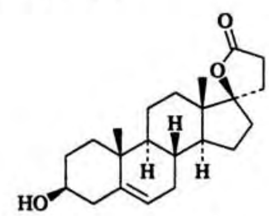
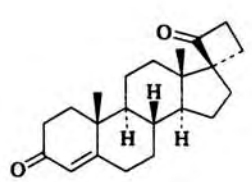
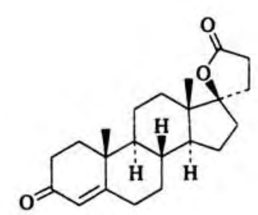
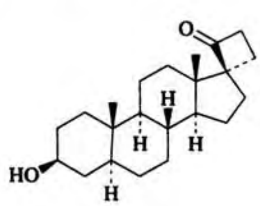
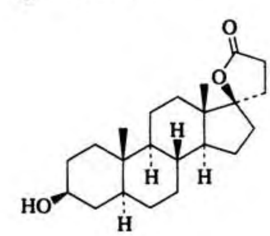
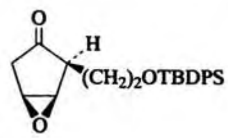
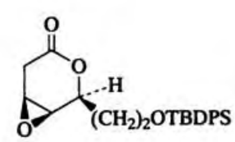
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{22}				
	30% H_2O_2, NaOH, CH_2OH, 2.25 h, 25°		(100)	188
	30% H_2O_2, NaOH, CH_3OH		(80)	187
	30% H_2O_2, NaOH, CH_3OH, 2 h, 25°		(75)	187
	30% H_2O_2, NaOH, CH_3OH, 1 h, 25°		(50)	187
	30% H_2O_2, NaOH, CH_3OH, 2 h, 25°		(100)	187
C_{23}				
	85% MCPBA, $NaHCO_3$, di(3-*t*-Bu-4-OH-5-$CH_3C_6H_2$) sulfide CH_2Cl_2, 24 h, heat		(>74)	160

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

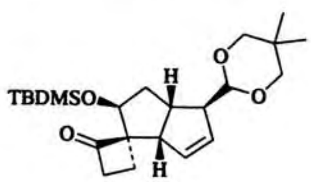
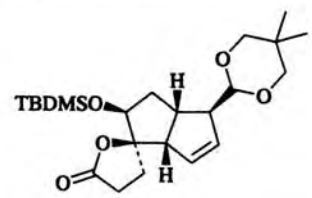
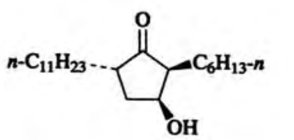
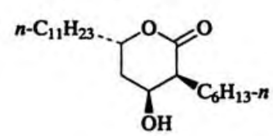
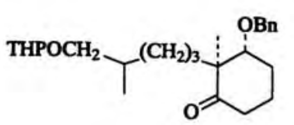
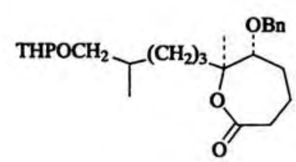
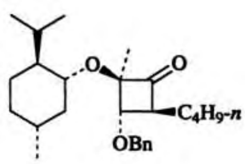
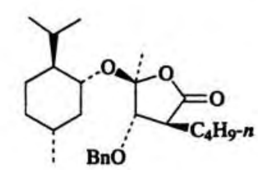
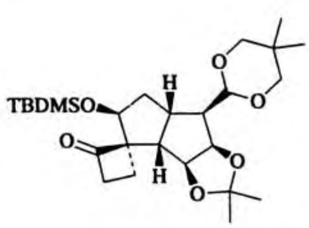
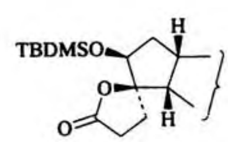
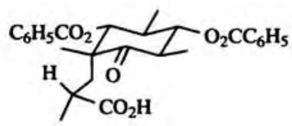
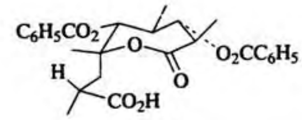
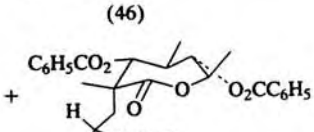
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2O_2, NaOH		(92)	194
	MCPBA, $NaHCO_3$, CH_2Cl_2, 20 h		(60)	209b
C_{25}				
	85% MCPBA, NaOAc, CH_2Cl_2, 17 h, heat		(70)	129, 952
C_{26}				
	H_2O_2, AcOH		(85)	198
	MCPBA, $NaHCO_3$, CH_2Cl_2, 0°		(78)	195
C_{27}				
	25% PAA, $CH_3CO_2C_2H_5$, 6 d, 55–58°	 (46) +  (minor)	(35)*	144

TABLE II. Reactions of Monocyclic and Spirocyclic Ketones (*Continued*)

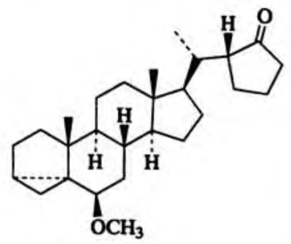
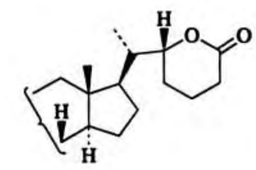
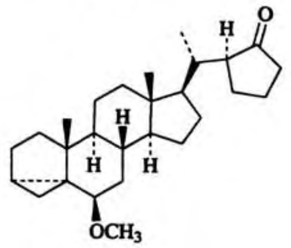
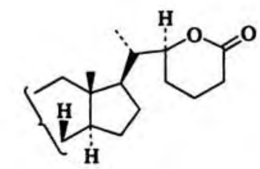
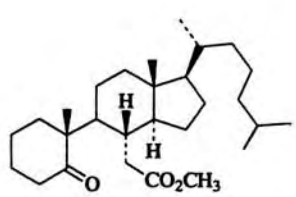
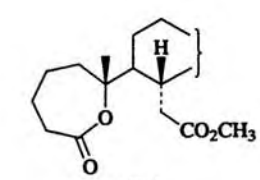
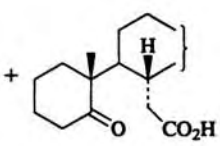
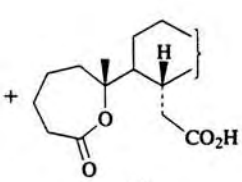
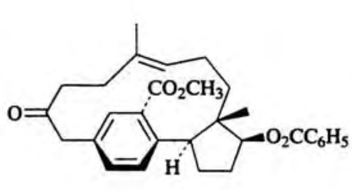
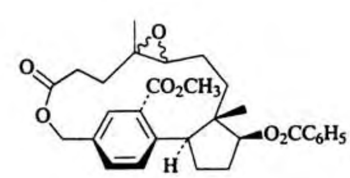
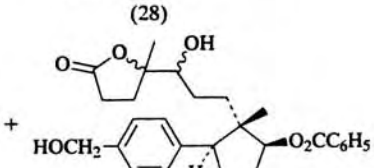
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2	 (—)	162
	MCPBA, $NaHCO_3$, CH_2Cl_2	 (—)	162
C_{28}			
	PBA, $CHCl_3$, 96 h, 25°	 (35) +  (8)	169
		+  (18) (10)*	
C_{30}			
	MCPBA, $NaHCO_3$, CH_2Cl_2, 10 d, 25°	 (28) +  (29)	953

TABLE II. REACTIONS OF MONOCYCLIC AND SPIROCYCLIC KETONES (*Continued*)

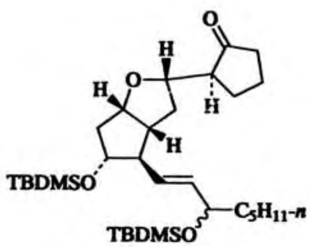
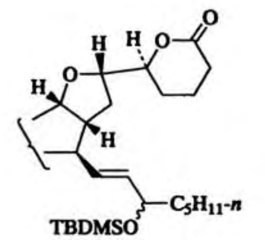
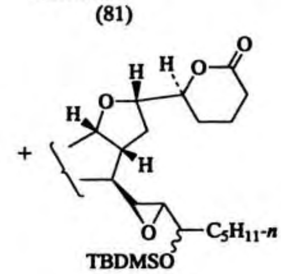
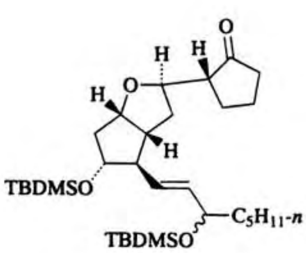
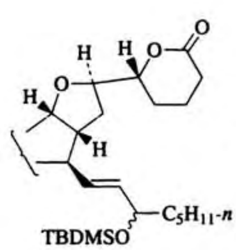
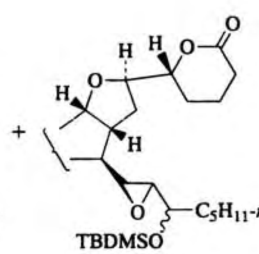
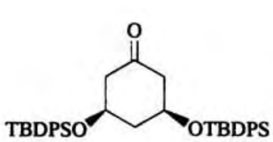
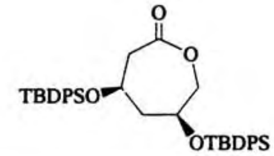
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{32}			
	MCPBA, $NaHCO_3$, CH_2Cl_2, 14 h, 0°	 (81) +  (14)	161
	MCPBA, $NaHCO_3$, CH_2Cl_2, 20 min, 0°, 72 h, −20°	 (83) +  (10)	161
C_{38}			
	MCPBA, $NaHCO_3$, CH_2Cl_2, 18 h	 (77)	136, 954

TABLE III. REACTIONS OF FUSED-RING KETONES

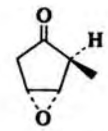
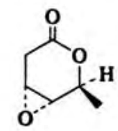
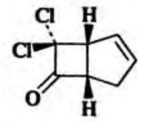
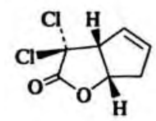
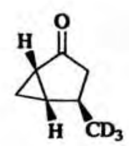
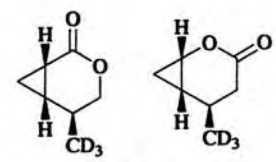
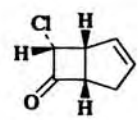
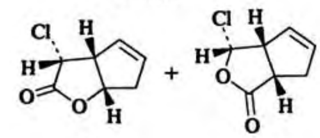
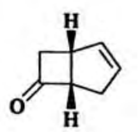
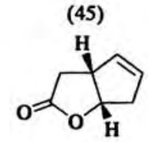
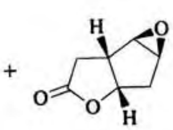
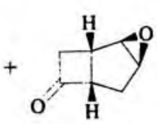
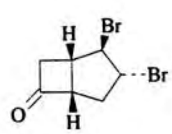
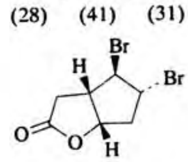
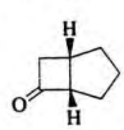
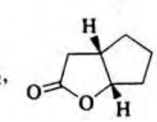
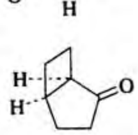
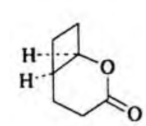
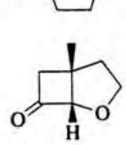
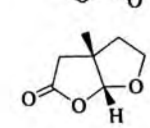
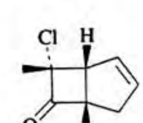
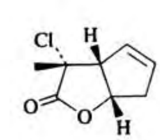
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°	 (98)	128
C_7 	H_2O_2, CF_3CH_2OH	 (56)	756
	MCPBA	 80:20 (61)	955
	30% H_2O_2, AcOH, 36 h, 5°	 (45) (19)	239
	30% H_2O_2, AcOH–H_2O, 12 h, 0°	 I (93)	220, 221, 233, 237, 756, 956, 957
	MCPBA	I +  II +  III (95) (3) (1)	230
	$Cl_3CCH_2CO_3H$, CH_2Cl_2, 25°	I + II + III (28) (41) (31)	230
	MCPBA	 (>77)	958
	$[(CH_3)_3Si]_2O_2$, $(CH_3)_3SiOS(O)_2CF_3$, CH_2Cl_2, 4.5 h, −40 to −35°	 (73)	221
	MCPBA, $CHCl_3$, 25°	 (40–90)	663, 664
	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 2 h, 25°	 (92)	959
C_8 	30% H_2O_2, NaOAc, AcOH (90%), 6 h, 10°	 (75)	226

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

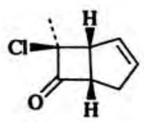
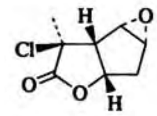
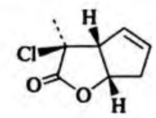
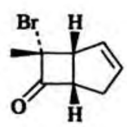
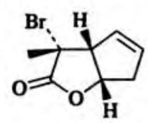
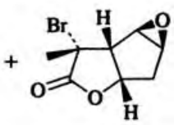
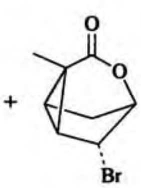
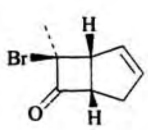
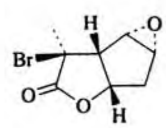
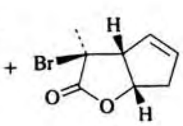
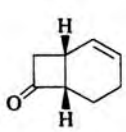
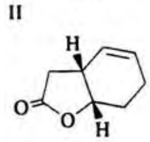
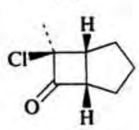
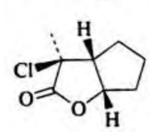
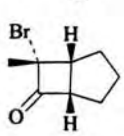
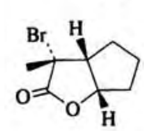
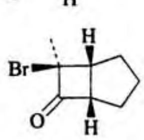
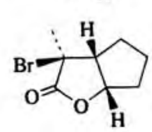
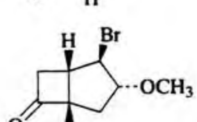
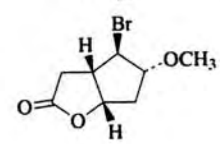
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	PAA, AcOH (glacial), 16 h	 I (8)  II (25)	226
	PAA, AcOH (90%), 16 h	II (36)	226
	30% H_2O_2, AcOH (90%), 24 h, 0°	II (27)	242
	MCPBA, $NaHCO_3$, $CHCl_3$, 3 h, 25°	 I (25) +  II (28)	226
	MCPBA, $NaHCO_3$, $CHCl_3$, 3 h, 5°	I (75)	226
	30% H_2O_2, AcOH	I (25) +  (15)	226
	MCPBA, $NaHCO_3$, $CHCl_3$, 24 h	 I (16) +  II (60)	226
	PAA, AcOH, 45 h	II (34)	226, 960
	30% H_2O_2, AcOH–H_2O, 16 h, 0–5°	 (95)	579, 961
	MCPBA, $NaHCO_3$, $CHCl_3$, 16 h	 (91)	226, 242, 960
	MCPBA, $NaHCO_3$, $CHCl_3$, 15 h	 (93)	226
	MCPBA, $NaHCO_3$, $CHCl_3$, 24 h, 25°	 (60)	226, 960
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (98)	226

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

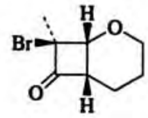
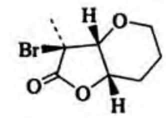
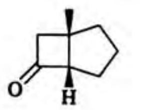
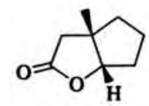
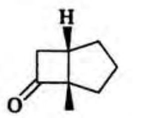
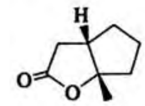
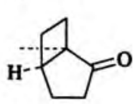
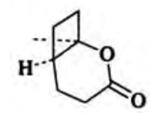
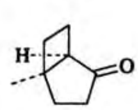
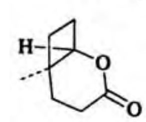
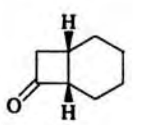
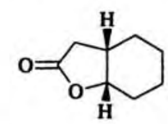
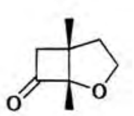
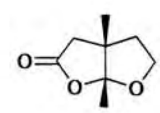
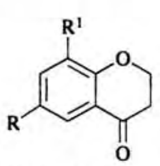
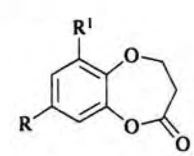
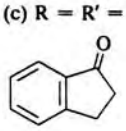
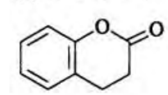
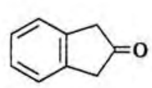
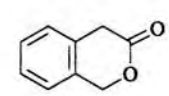
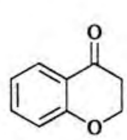
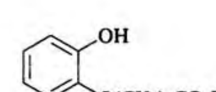
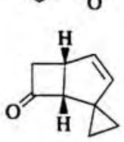
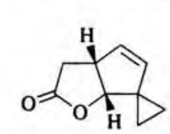
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, $CHCl_3$, 16 h	 (65)	226
	H_2O_2, NaOH, 0°	 (100)	656, 962, 963
	H_2O_2, NaOH	 (100)	656
	MCPBA, $CHCl_3$, 25°	 (40–90)	663, 664
	MCPBA, $CHCl_3$, 25°	 (40–90)	663, 664
	30% H_2O_2, NaOH, 2 h, 25°	 (>60)	962, 963
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 h, 25°	 (90)	959
C_9			
	MCPBA, CH_2Cl_2, 15–18 h, heat		964
(a) R = Cl, R′ = H		(a) R = Cl, R′ = H (61)	
(b) R = Br, R′ = H		(b) R = Br, R′ = H (59)	
(c) R = R′ = H		(c) R = R′ = H (60)	
	MCPBA, H_2SO_4/Ac_2O, CH_2Cl_2, 12 d, 25°	 (71)	763a, 965, 966, 967
	MCPBA, CH_2Cl_2, 10 d, 0°	 (90)	752, 763a, 968, 969
	MCPBA, CF_3CO_2H, CH_2Cl_2, 8 h, 0–25°	" (71)	742
	30% H_2O_2, $HClO_4$, 4 d, 20°	 (95)	970
	1. 30% H_2O_2, AcOH–H_2O, 1.5 h, −2 to 2° 2. 35 h, 5°	 (54)	971

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

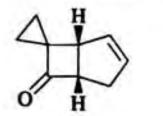
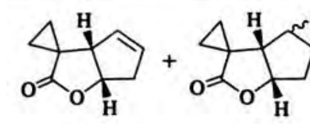
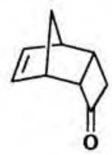
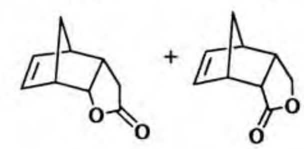
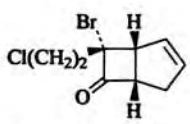
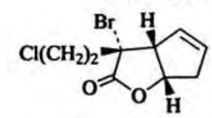
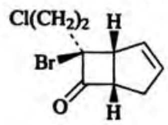
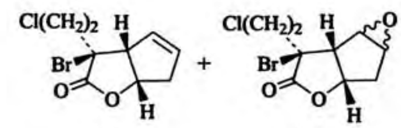
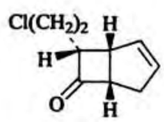
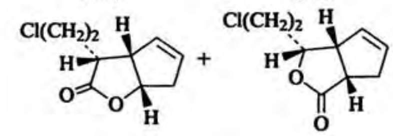
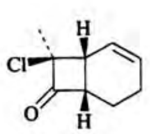
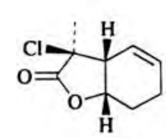
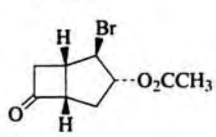
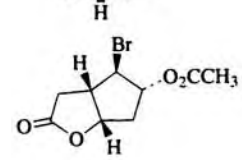
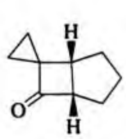
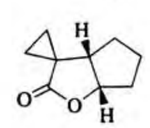
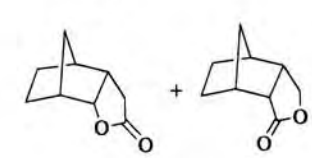
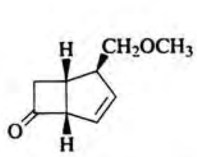
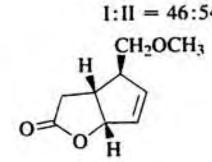
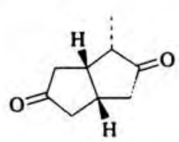
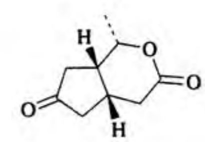
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (40) (20)	238
	30% H_2O_2, NaOH, CH_3OH, 2.5 h, 25°	 I II I:II = 31:69 (60)	243
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (70)	238
	MCPBA, $NaHCO_3$, $CHCl_3$, 4 d, 25°	 (50) (25)	238
	CPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 I II I:II = 40:60 (40)	238
	30% H_2O_2, AcOH (90%), 24 h, 0°	 (59)	242
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (97)	238
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (96)	238
	30% H_2O_2, NaOH, CH_3OH	 I II I:II = 46:54 (—)	243
	H_2O_2, AcOH–H_2O, 72 h, 0°	 (66)	972
	MCPBA, $NaHCO_3$, CH_2Cl_2, 7 d	 (66)	636

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

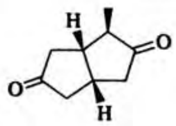
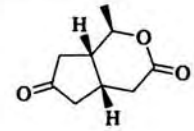
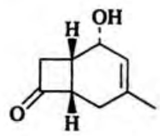
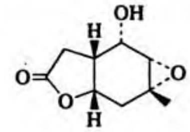
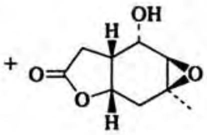
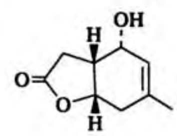
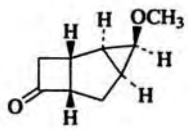
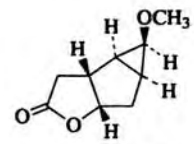
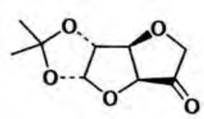
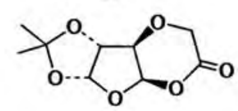
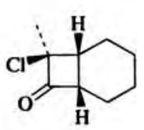
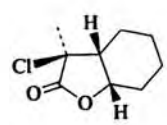
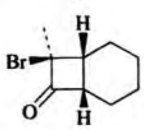
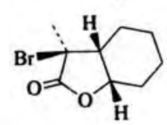
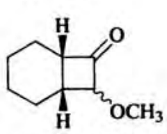
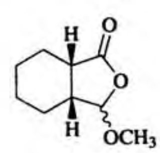
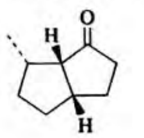
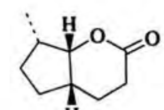
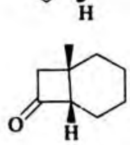
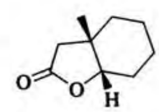
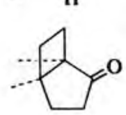
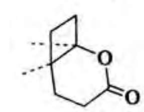
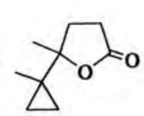
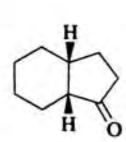
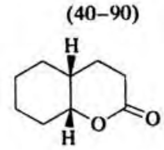
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 7 d	 (66)	636
	MCPBA, $NaHCO_3$, CH_2Cl_2, 15 h, 0–5°	 I +  II (84) I:II = 75:25	247, 248
	30% H_2O_2, AcOH–H_2O, 20 h, 4°	 (75)	247, 248
	30% H_2O_2, AcOH, 16 h, 5–10°	 (>90)	233
	MCPBA, $CHCl_3$, <2 h, 25°	 (75)	301
	30% H_2O_2, AcOH–H_2O, 24 h, 0°	 (90)	242
	MCPBA, $NaHCO_3$, CH_2Cl_2, 20 h	 (63)	226, 960
 *exo:endo* = 85:15	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 (79)	198a
	80% MCPBA, CH_2Cl_2, 48 h, 25°	 (76)	261
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 15 min, 0° 2. 21 h, 25°	 (90)	962, 963
	MCPBA, $CHCl_3$, 25°	 (40–90) +  trace	663, 664
	TFPAA, Na_2HPO_4, CH_2Cl_2, 7 h, 25°	 (55)	928

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

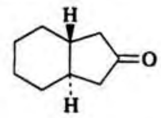
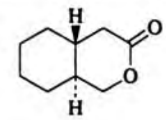
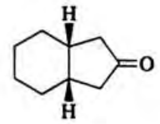
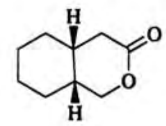
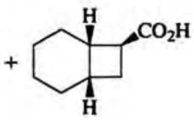
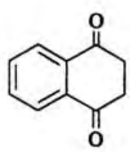
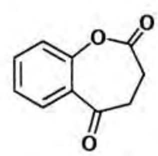
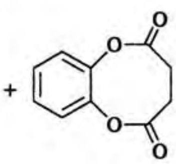
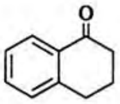
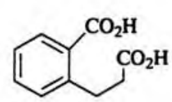
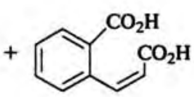
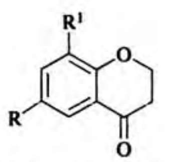
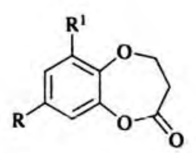
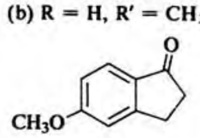
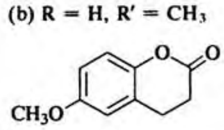
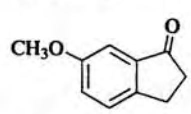
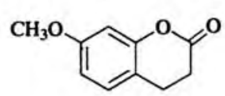
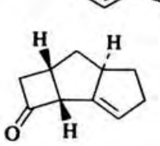
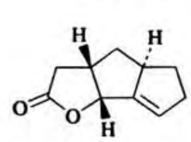
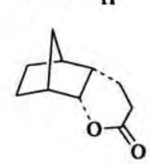
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	34% H_2O_2, SeO_2, *t*-BuOH, 7 h, 80°	 (70) +(20)*	679
	TFPAA (85%), 10 min	" (68)	973
	34% H_2O_2, SeO_2, *t*-BuOH, 7 h, 80°	 +  I (50) II (30) +(20)*	679
	MCPBA (85%), CF_3CO_2H, CH_2Cl_2, 6 h, 0–25°	I (96)	742
C_{10}			
	1. TFPAA, NaH_2PO_4, CH_2Cl_2, 6 h, 0° 2. 12 h, 25°	 +  (—)	318
	*t*-BuO_2H, KOH, 80°	 (5) +  (1) (—)	532
 (a) R = CH_3, R′ = H (b) R = H, R′ = CH_3	MCPBA, CH_2Cl_2, 15–18 h, heat	 (a) R = CH_3, R′ = H (62) (b) R = H, R′ = CH_3 (60)	964
	MCPBA, H_2SO_4–Ac_2O, CH_2Cl_2, 14 d, 25°	 (71)	965
	MCPBA, H_2SO_4–Ac_2O, CH_2Cl_2, 10 d, 25°	 (80)	965
	30% H_2O_2, AcOH–H_2O, 0°	 (65)	225
	MCPBA, CH_2Cl_2, 24 h, heat	 +  I II I:II = 75:25 (74)	260
	30% H_2O_2, AcOH, 2 h, 50°	I:II = 100:0 (87)	222, 974

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

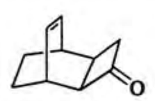
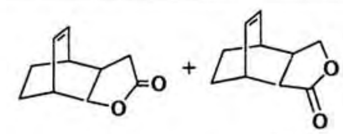
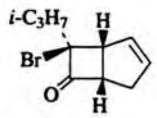
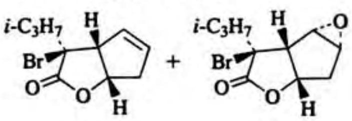
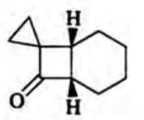
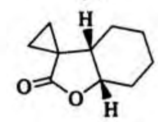
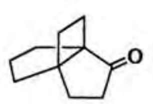
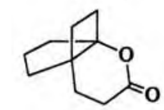
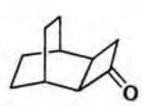
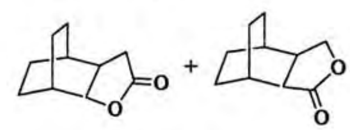
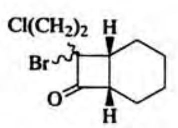
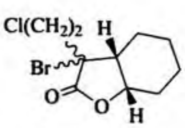
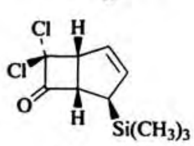
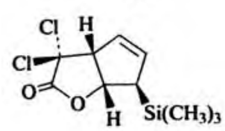
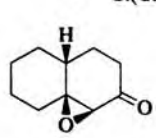
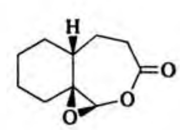
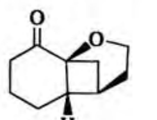
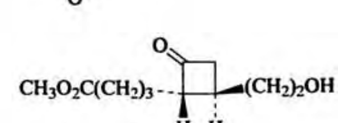
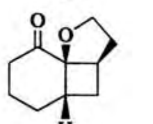
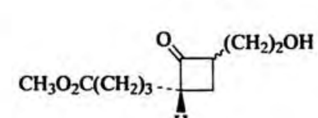
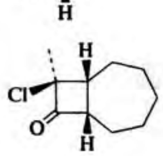
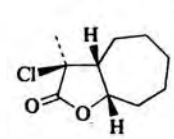
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, NaOH, CH_3OH, 2.5 h, 25°	 I II I:II = 46:54 (76)	243, 244
	PAA, AcOH, 120 h	 (6) (4)	226, 960
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 (70)	238
	30% H_2O_2, AcOH, 25°	 (35–80)	663, 664
	30% H_2O_2, NaOH, CH_3OH, 25°	 I II I:II = 62:38 (—)	243, 244
	MCPBA, $NaHCO_3$, $CHCl_3$, 12 h, 25°	 (70)	238
	30% H_2O_2, AcOH, 3 d, 0–5°	 (82)	972, 975
	MCPBA, CH_2Cl_2, 72 h, 25°	 (71)	298
	MCPBA, CH_2Cl_2, 30 min, 25°	 (83)	976
	MCPBA, CH_2Cl_2, 3.5 h, 25°	 (83)	976
	30% H_2O_2, AcOH–H_2O, 24 h, 0°	 (77)	242

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

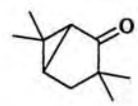
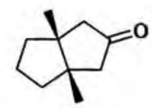
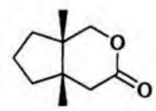
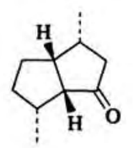
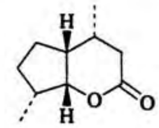
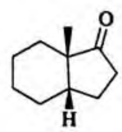
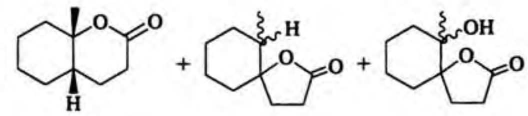
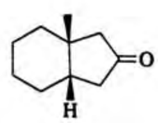
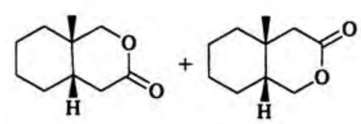
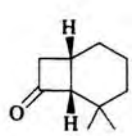
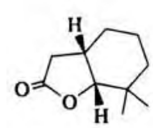
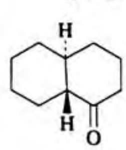
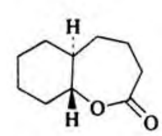
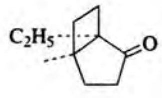
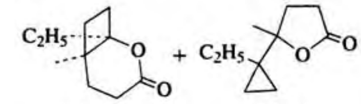
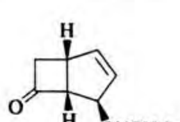
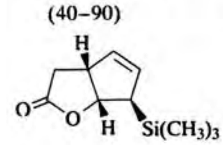
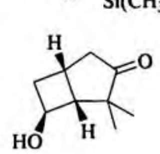
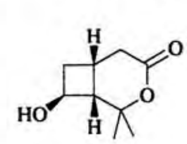
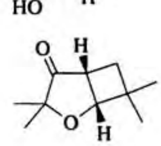
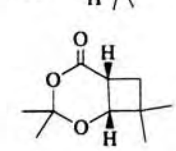
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2	(0)	943
	MCPBA, CH_2Cl_2, 20 h, reflux	 (98)	977
	MCPBA, CH_2Cl_2, 5 h, 25°	 (40)	700
	PAA, H_2SO_4, AcOH, 5 d, 25°	 I (40) + II (32) + III (28)	667
	40% PAA, NaOAc, AcOH, 5 d, 25°	I (94)	667
	75% MCPBA, $CHCl_3$, 2.5 d, 25°	 I + II (74); I:II = 60:40	267
	TFPAA	 (—)	978
	$C_6H_5SeO_3H$, Na_2HPO_4, CH_2Cl_2, 2.5 h	 (79)	222
	MCPBA, $CHCl_3$, 25°	 (40–90) + (trace)	663, 664
	H_2O_2, NaOH, CH_3OH, 2 h, 25°	 (83)	972
	MCPBA, $NaHCO_3$, 12 h, 25°	 (95)	258, 979
	MCPBA, $NaHCO_3$, CH_2Cl_2, 15 h, 25°	 (>87)	254

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

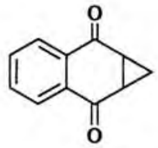
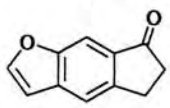
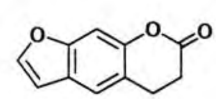
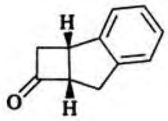
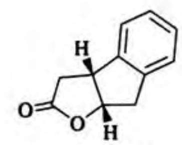
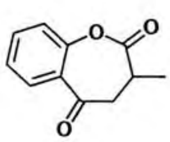
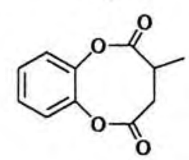
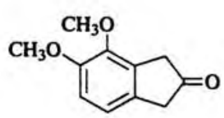
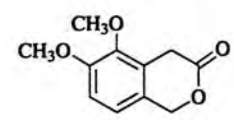
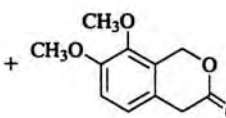
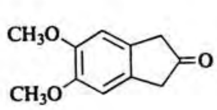
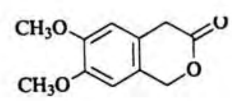
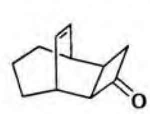
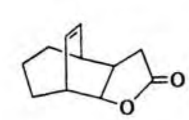
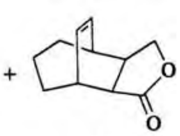
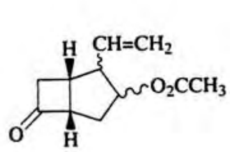
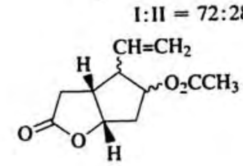
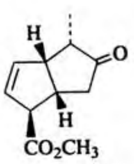
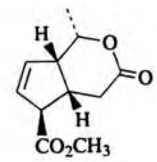
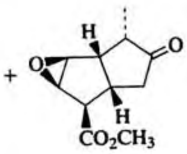
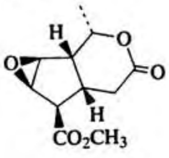
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	TFPAA, NaH_2PO_4, CH_2Cl_2, 6 h, heat, 12 h, 25°	(0)	318
	30% H_2O_2, H_2SO_4–Ac_2O, CH_2Cl_2, 30 min, 25°	 (71)	315
	TFPAA (98%), K_2HPO_4, CH_2Cl_2, 24 h, 25°	 (64)	962
	TFPAA, NaH_2PO_4, CH_2Cl_2, 6 h, heat, 12 h, 25°	 (20)	318
	MCPBA, CH_2Cl_2, 2 d, 25°	 I +  II (43) I:II = 60:40	263
	MCPBA, CH_2Cl_2, 10 d, 0°	 (64)	968
	30% H_2O_2, NaOH, CH_3OH, 2.5 h, 25°	 I +  II (85) I:II = 72:28	243, 244
	MCPBA, $NaHCO_3$	 (93)	980
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 (70) +  (12) +  (10)	227, 228

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

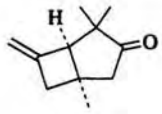
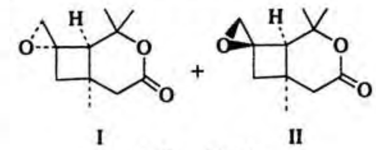
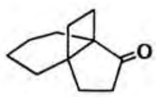
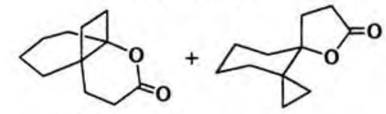
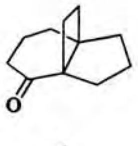
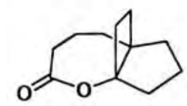
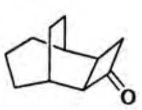
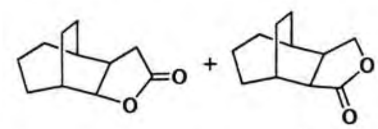
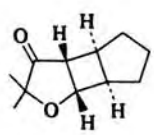
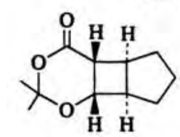
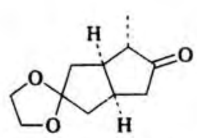
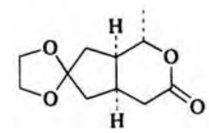
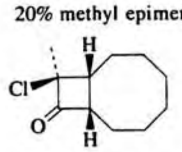
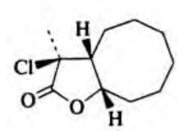
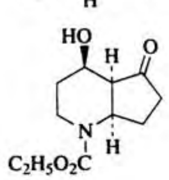
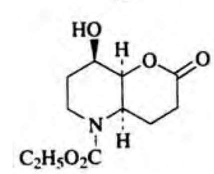
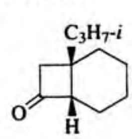
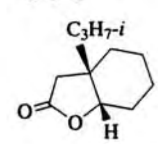
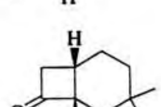
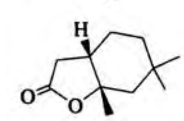
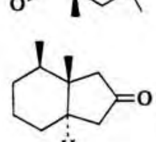
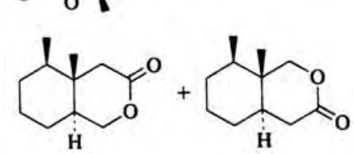
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 I + II; I:II = 88:12 (100)	259
	30% H_2O_2, AcOH, 25°	 (35–80) + (10)	663, 664
	MCPBA, $CHCl_3$, 6 d, 25°	 (96)	981
	30% H_2O_2, NaOH, CH_3OH, 2.5 h, 25°	 I + II; I:II = 82:18 (—)	243, 244
	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°	 (91)	982
 20% methyl epimer	MCPBA, $NaHCO_3$, CH_2Cl_2	 (90)	983
	30% H_2O_2, AcOH–H_2O, 24 h, 0°	 (87)	242
	1. TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 0° 2. 2 h, 25°	 (50)	85
	TFPAA (98%), K_2HPO_4, CH_2Cl_2, >10 min, 0°	 (71)	962
	TFPAA	 (—)	978
	MCPBA, CH_2Cl_2	 I + II; I:II = 23:77 (—)	265

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

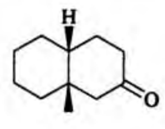
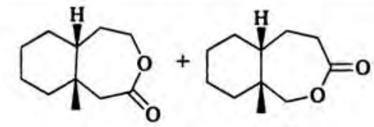
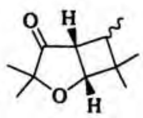
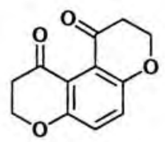
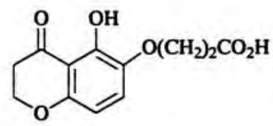
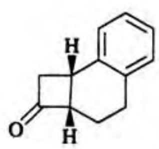
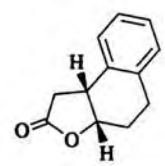
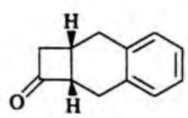
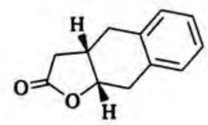
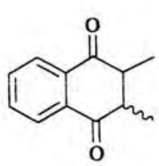
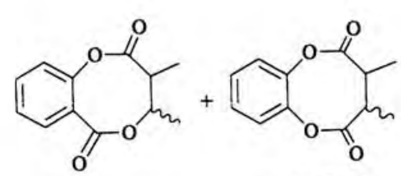
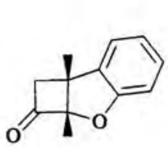
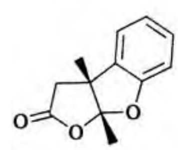
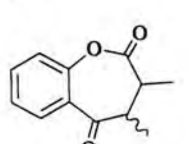
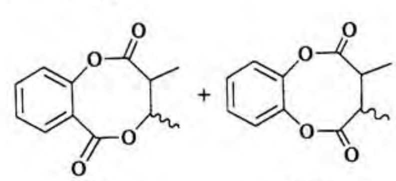
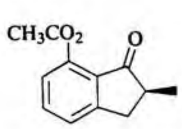
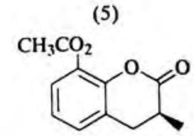
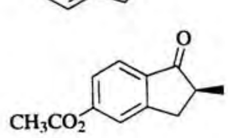
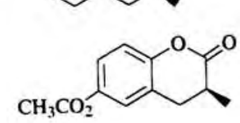
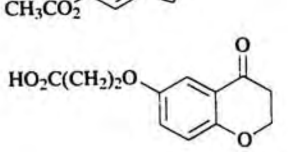
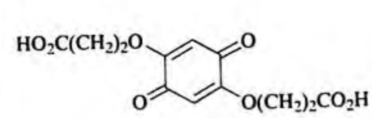
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	75% MCPBA, $CHCl_3$, 2 d, 25°	 I + II; I:II = 19:81 (91)	267
	MCPBA	(0)	254
C_{12}			
	30% H_2O_2, $HClO_4$, 2 d, 20°	 (68)	970
	TFPAA (98%), K_2HPO_4, CH_2Cl_2, 20 h, 25°	 (59)	962
	TFPAA (98%), K_2HPO_4, CH_2Cl_2, 19 h, 25°	 (64)	962
	TFPAA, NaH_2PO_4, CH_2Cl_2	 not isolated (trace)	318
	85% MCPBA, $NaHCO_3$, CH_2Cl_2, 2 h, 25°	 (92)	959
	TFPAA, NaH_2PO_4, CH_2Cl_2	 (5) + trace	318
	TFPAA, NaH_2PO_4, CH_2Cl_2, 12 h, heat	 (88)	316
	TFPAA, NaH_2PO_4, CH_2Cl_2, 12 h, heat	 (80–85)	316
	30% H_2O_2, $HClO_4$, 3 d, 20°	 (78)	970

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

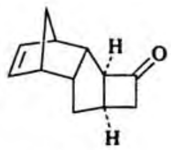
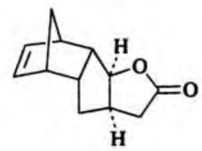
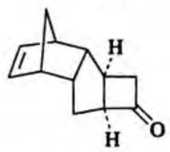
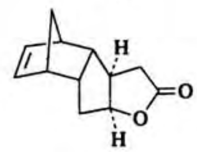
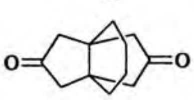
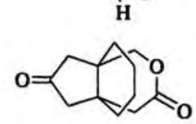
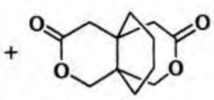
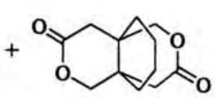
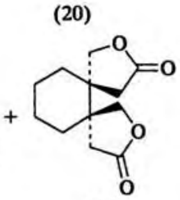
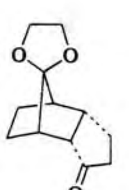
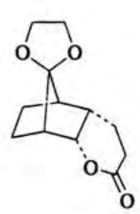
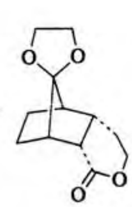
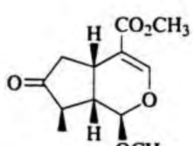
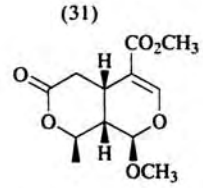
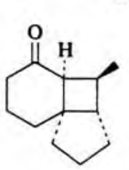
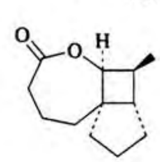
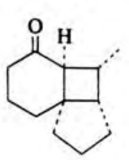
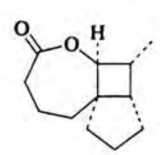
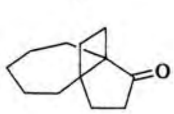
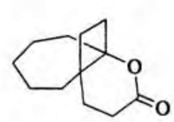
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2O_2, AcOH, 24 h, 0°		(95)	984, 985
	H_2O_2, AcOH, 24 h, 0°		(95)	984, 985
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25 d, 25°	 I (12) +  II (20) +  III (26) +  IV (11)		660
	MCPBA, TsOH, CH_2Cl_2, 25 d, 25°	II (35) + IV (46)		660
	MCPBA, TsOH, benzene, 36 h, 25°	 (31) +  (25)		986
	MCPBA, $NaHCO_3$, CH_2Cl_2, 20 h, 25°		(50–60)	257
	MCPBA, $CHCl_3$, 12 h, 25°		(70)	987
	MCPBA, $CHCl_3$, 12 h, 25°		(70)	987
	30% H_2O_2, AcOH, 25°		(35–80)	663, 664

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

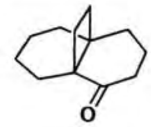
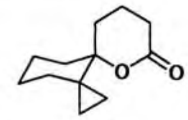
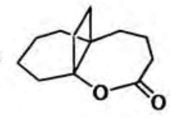
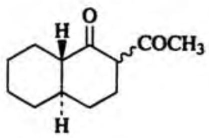
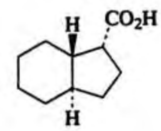
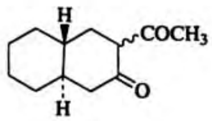
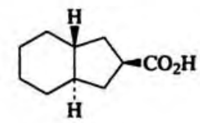
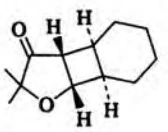
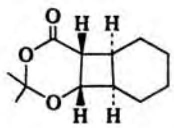
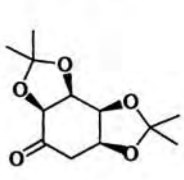
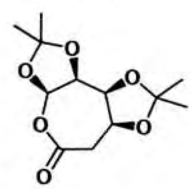
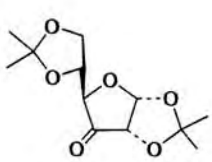
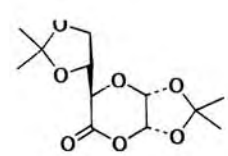
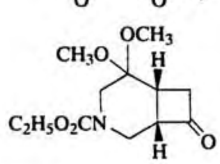
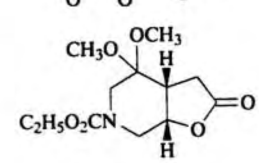
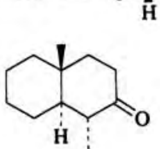
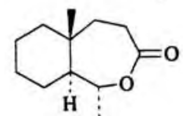
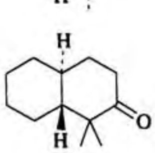
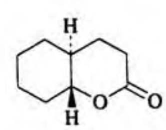
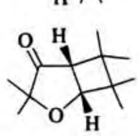
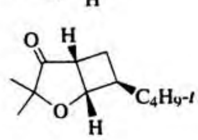
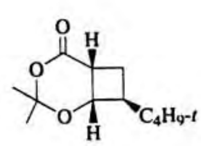
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $CHCl_3$, 6 d, 25°	 (52) +  (32)		981
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(92)	82
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(81)	81
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°		(99)	982
	PBA, $CHCl_3$ (moist)		(84)	291
	MCPBA, $CHCl_3$, <2 h, 25°		(65)	301
	MCPBA, CH_2Cl_2, 2.5 d, 25°		(>61)	232
	$C_6H_5SeO_3H$, Na_2HPO_4, CH_2Cl_2, 2 h		(50) (45)*	222
	40% PAA, BF_3, CH_2Cl_2, 16 h, 6°		(36)	284
	MCPBA		(0)	254
	MCPBA		(>67)	254

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

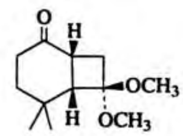
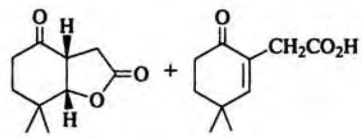
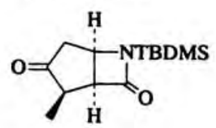
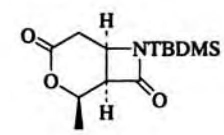
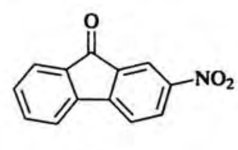
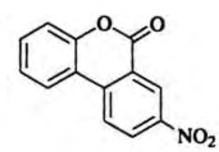
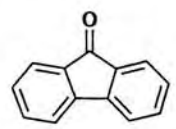
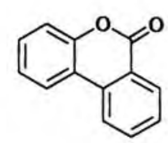
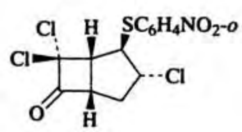
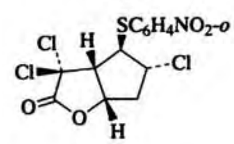
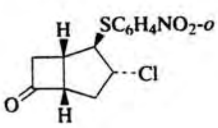
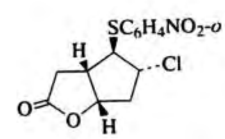
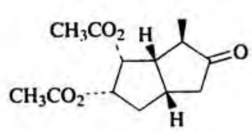
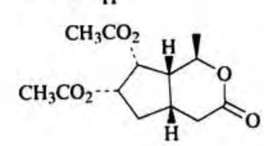
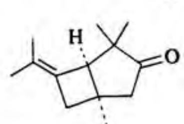
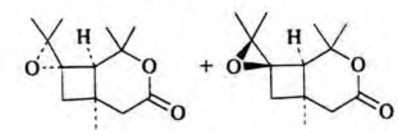
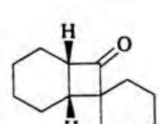
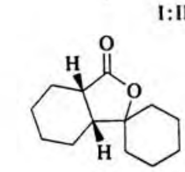
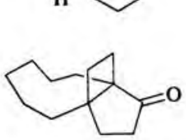
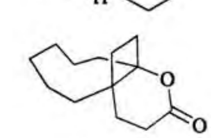
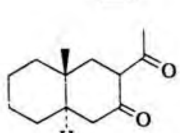
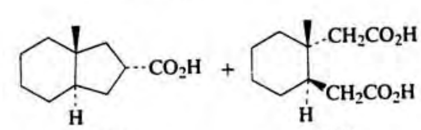
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, AcOH, 6–7 h, 25°	 (81) No ratio	111
	MCPBA, $NaHCO_3$, CH_2Cl_2, 40°	 (98)	264
C_{13}			
	40% PAA, H_2SO_4, AcOH, 4.5 h, 0–25°	 (48)	319
	30% H_2O_2, AcOH, 72 h, 50°	 (85)	14, 47, 319, 751, 763a, 974
	85% MCPBA, $CHCl_3$, 1 h, heat	 (91)	988
	85% MCPBA, $CHCl_3$, 2 h, heat	 (86)	988
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 (83)	228
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 I + II (100) I:II = 95:5	259
	30% H_2O_2, NaOH, CH_3OH, 4 h, 25°	 (85)	152
	30% H_2O_2, AcOH, 25°	 (35–80)	663, 664
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°	 (63) + (14)	81

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

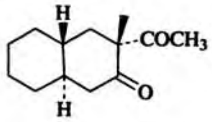
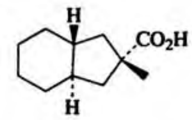
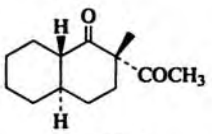
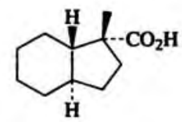
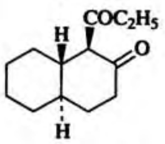
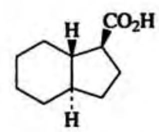
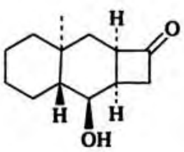
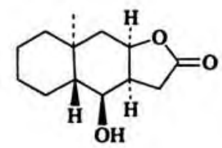
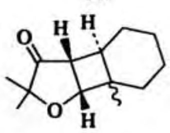
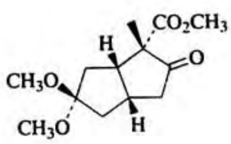
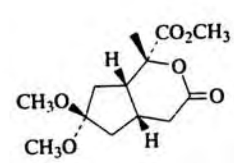
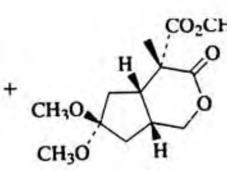
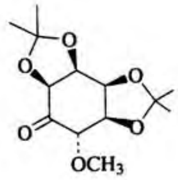
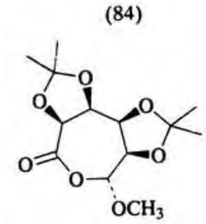
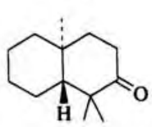
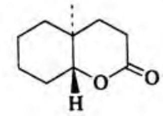
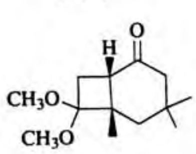
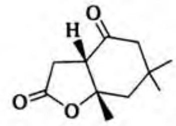
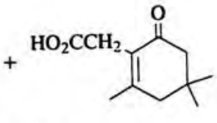
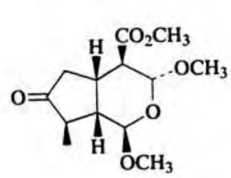
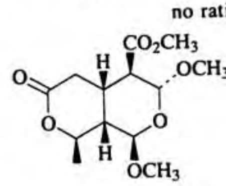
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(91)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH, 24 h, 25°		(93)	81
	30% H_2O_2, H_2SO_4, *t*-BuOH 24 h, 25°		(—)	81
	30% H_2O_2, AcOH, 15 h, 5°		(>90)	989
	MCPBA		(0)	254
	MCPBA, $NaHCO_3$, CH_2Cl_2, 14 d, 25°	 (84) +  (7)		636
	PBA, $CHCl_3$ (moist)		(80)	300
	40% PAA, BF_3, CH_2Cl_2, 16 h, 6°		(41)	284
	30% H_2O_2, AcOH, 6–7 h, 25°	 +  no ratio	(60)	111
	MCPBA, $NaHCO_3$, CH_2Cl_2, 4 h, 25°		(60–70)	257

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

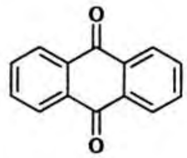
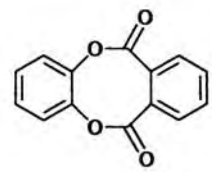
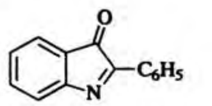
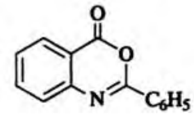
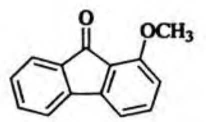
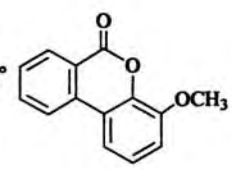
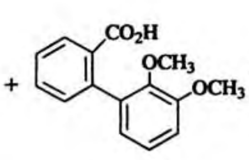
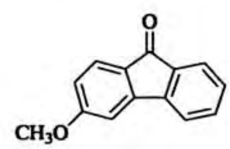
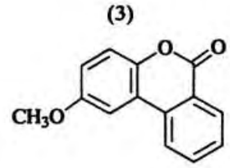
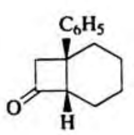
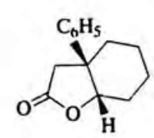
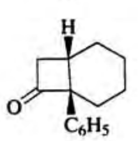
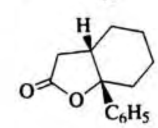
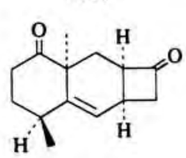
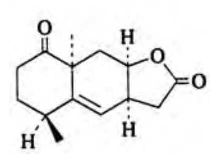
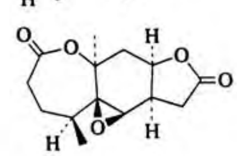
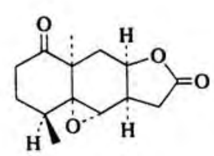
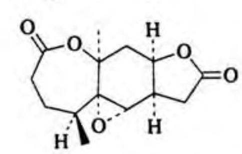
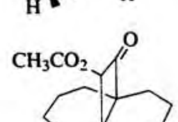
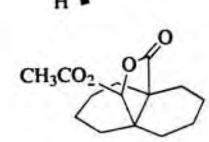
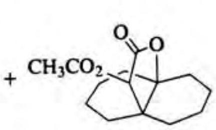
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	TFPAA, NaH_2PO_4, CH_2Cl_2, 6 h, heat, 12 h, 25°	 (low)	318
	85% MCPBA, $CHCl_3$, 12 h, 25°	 (71)	645
	1. PAA, H_2SO_4, AcOH, 4 h, 25° 2. $(CH_3)_2SO_4$, NaOH	 (3) +  (58) (3)*	319
	40% H_2O_2, H_2SO_4, AcOH, 4 h, 25°	 (80)	319
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 21 h, 25°	 (93)	962
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 21 h, 25°	 (82)	962, 963
	*t*-BuO_2H, NaOH, THF, 30 min, 0°	 (83)	223, 235
	MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h, 25°	 (80)	223, 235
	MCPBA, Li_2CO_3, 4,4′-thiobis(2-*tert*-butyl-6-methylphenol), 7 d, heat	 (64) +(22)*	223
	MCPBA, $CHCl_3$, 20°	 I +  II (98) I:II = 20:80	294

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

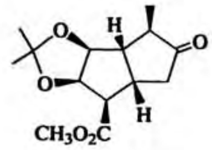
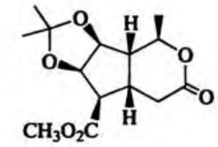
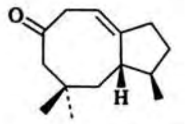
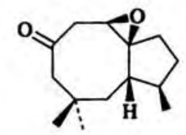
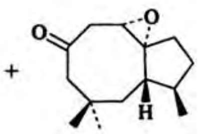
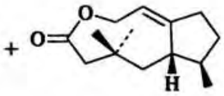
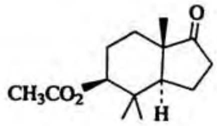
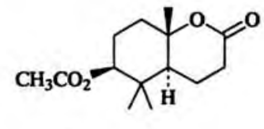
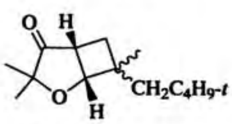
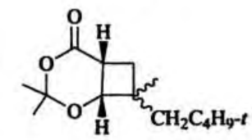
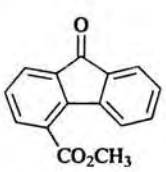
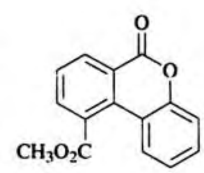
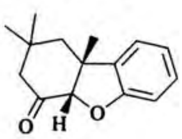
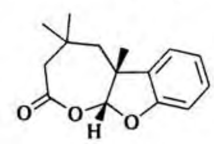
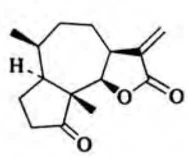
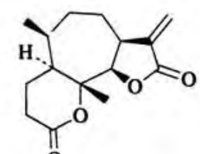
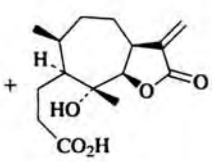
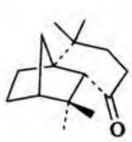
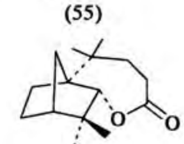
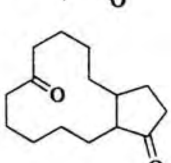
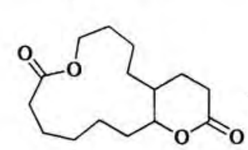
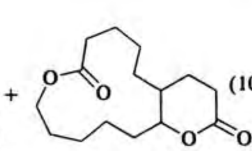
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 12 h, 25°	 (99)	227, 228
	MCPBA, CH_2Cl_2	 +  +  (—)	990
	TFPAA, Na_2HPO_4, CH_2Cl_2	 (70)	991
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°	 (99)	982
C_{15}			
	1. 40% PAA, H_2SO_4, AcOH, 1 h, 0–10° 2. 3 h, 25°	 (83)	319
	MCPBA, CH_2Cl_2, 20 h, 25°	 (97)	992, 993
	30% H_2O_2, $C_6H_5SeO_2H$, *t*-BuOH, 17 h, 40°	 (55) +  (20)	222, 262
	30% H_2O_2, AcOH, 7 h, 50°	 (96)	974
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	 +  (100)	849

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

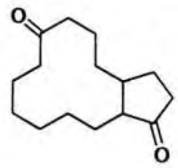
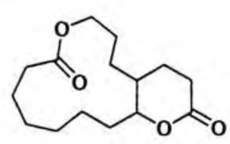
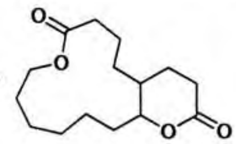
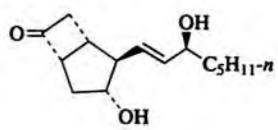
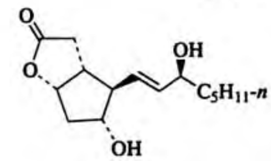
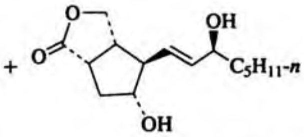
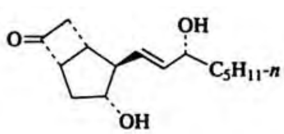
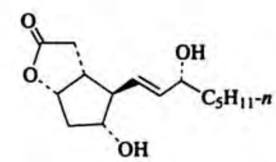
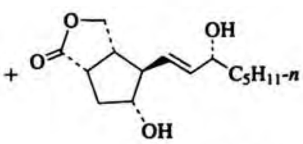
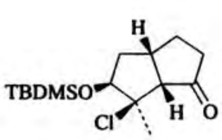
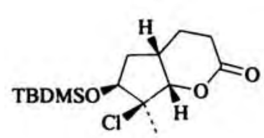
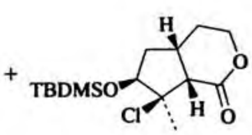
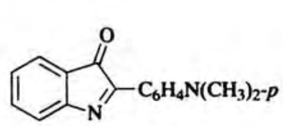
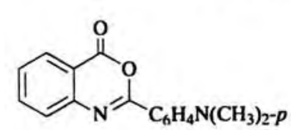
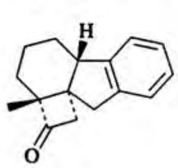
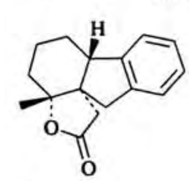
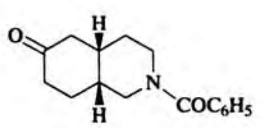
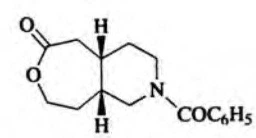
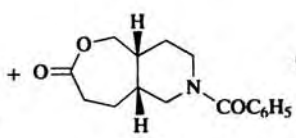
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	 I +  II (—) I:II = 50:50	849
	40% PAA, NaOAc, CH_2Cl_2, 16 h, −20°	 I +  II (100) I:II = 91:9	229, 994
	40% PAA, NaOAc, CH_2Cl_2, 4 d, −78°	I:II = 97:3 (100)	229
	MCPBA, $NaHCO_3$, CH_2Cl_2, 4 h, −78°	I:II = 100:0 (86)	231
	40% PAA, NaOAc, CH_2Cl_2, −78°	 I +  II (91) I:II = 96:4	229
	MCPBA	 I +  II (—) I:II = 80:20	701
C_{16}			
	35% H_2O_2, DMF, 15 h, 25°	 (60)	644
	30% H_2O_2, C_2H_5OH, 20 h, 25°	 (84)	995
	95% MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h, 25°	 (36) +  (57)	996

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

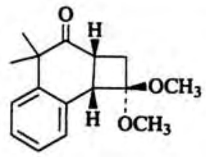
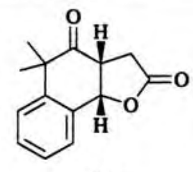
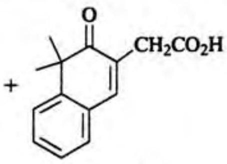
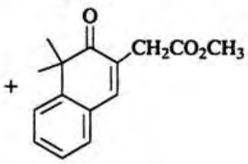
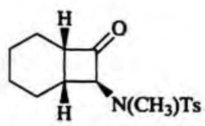
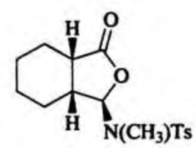
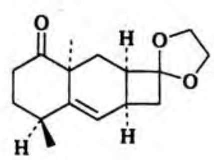
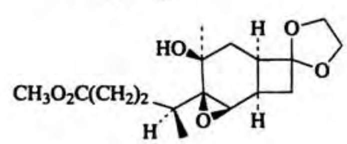
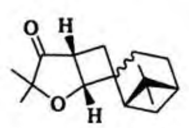
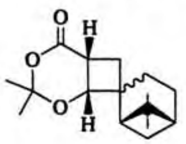
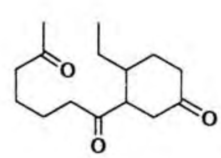
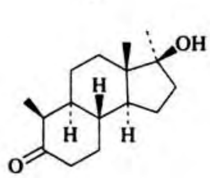
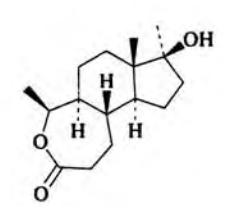
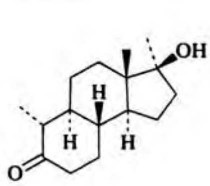
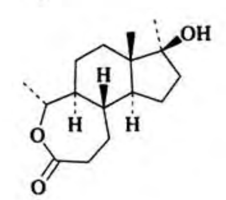
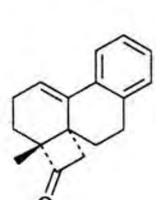
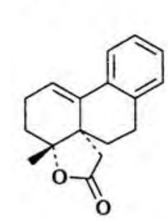
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, AcOH, 3 h, 25°	 (7) +  (45) +  (24)	111
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 (92)	198a
	1. MCPBA (2 eq), $NaHCO_3$, CH_2Cl_2, 30 h, 25° 2. K_2CO_3, CH_3OH	 (80)	272
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°	 (99)	982
	TFPAA	$HO_2C(CH_2)_4CO_2H$ + $HO_2C(CH_2)_3CO_2H$ + $HO_2C(CH_2)_2CO_2H$ (—)	849
	MCPBA, $CHCl_3$, 24 h, 25°	 (70)	997
	MCPBA, $CHCl_3$, 24 h, 25°	 (70)	997
C_{17}			
	30% H_2O_2, NaOH, 21 h, 25°	 (87)	995

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

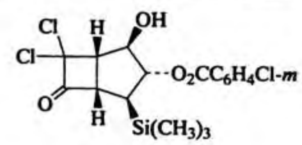
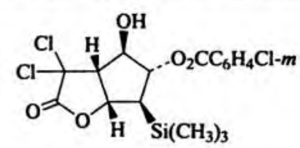
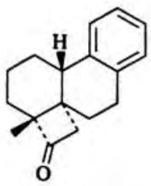
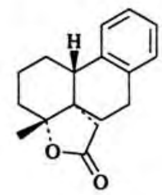
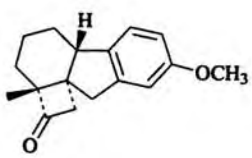
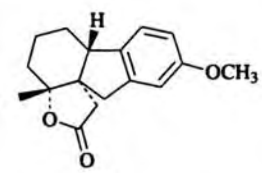
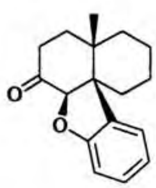
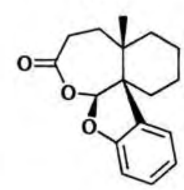
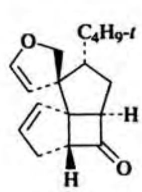
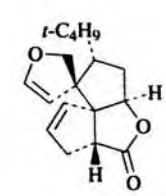
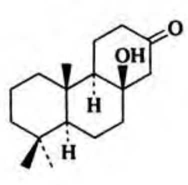
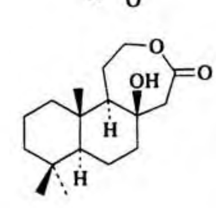
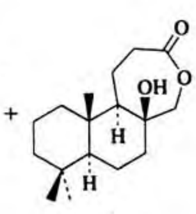
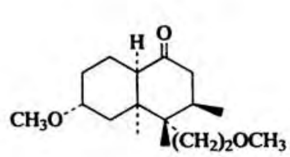
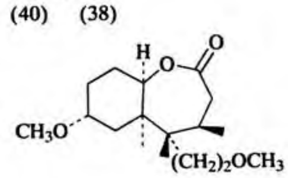
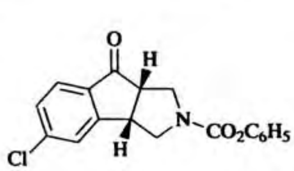
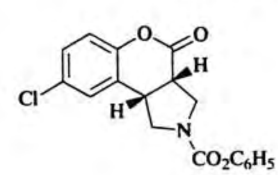
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, AcOH, 4 d, 25°	 (31)	972
	30% H_2O_2, NaOH, C_2H_5OH, 20 h, 25°	 (75)	995
	30% H_2O_2, NaOH, C_2H_5OH, 20 h, 25°	 (75)	995
	MCPBA, CH_2Cl_2, 20 h, 25°	 (75)	992
	$(C_6H_5)_3CO_2H$, NaOH, acetone, 2.15 h, −30°	 (86)	249, 250
	MCPBA, $CHCl_3$, 4,4′-thiobis(6-*tert*-butyl-3-methylphenol), 16 h, heat	 I (34) +  II (49)	305
	MCPBA, CH_2Cl_2, 9 d, 3°	I (51) + II (28)	304
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, 0° and 3 h, 20°	I (40) + II (38)	304
	TFPAA	 (72)	271
C_{18}			
	30% H_2O_2, H_2SO_4, AcOH, 16 h, 10–20°	 (61)	317

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

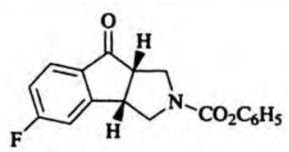
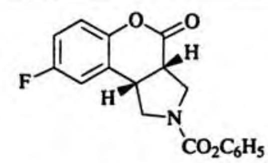
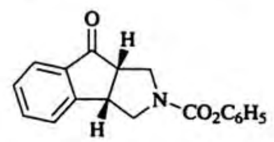
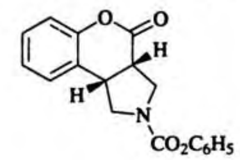
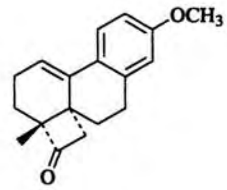
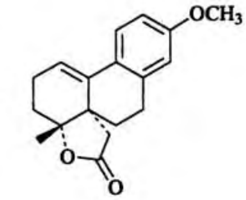
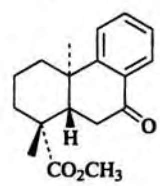
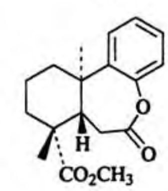
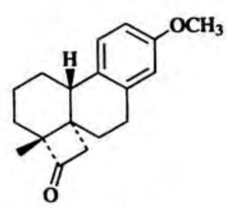
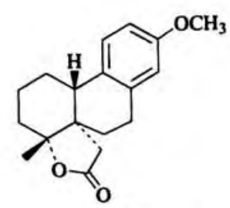
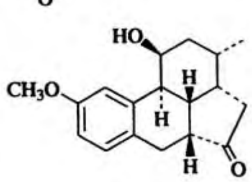
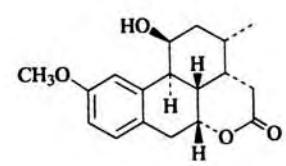
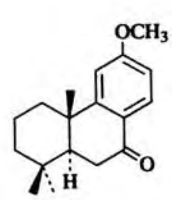
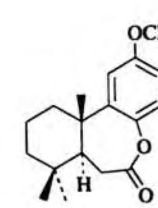
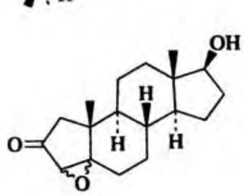
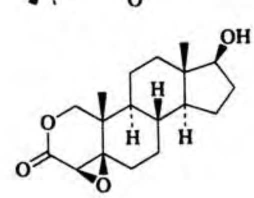
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, H_2SO_4, AcOH, 16 h, 10–20°	 (89)	317
	30% H_2O_2, H_2SO_4, AcOH, 16 h, 10–20°	 (76)	317
	30% H_2O_2, NaOH, 21 h, 25°	 (67)	995
	TFPAA, Na_2HPO_4, CH_2Cl_2, 20 min, 25°	 (61)	998
	30% H_2O_2, NaOH, C_2H_5OH, 20 h, 25°	 (71)	995
	MCPBA, TsOH, CH_2Cl_2, 5 h, 25°	 (68)	255, 256
	TFPAA, CH_2Cl_2, 70 h, 25°	 (98)	116, 117
	30% H_2O_2, NaOH, *t*-BuOH, 2 d, 25°	 (51)	299

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

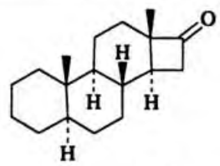
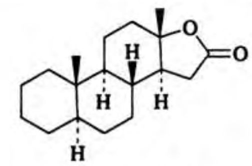
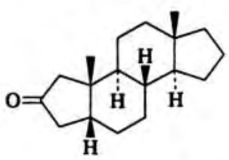
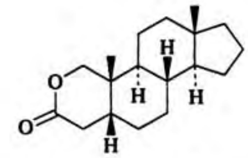
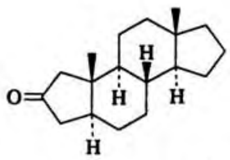
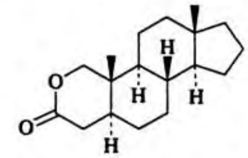
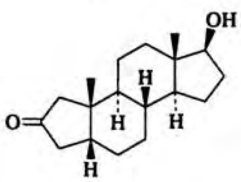
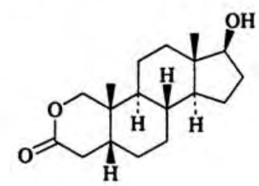
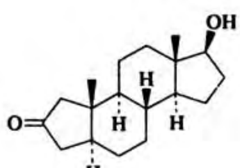
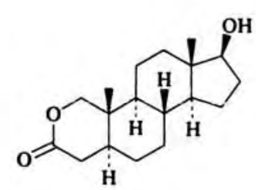
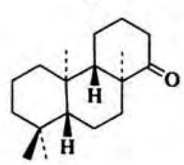
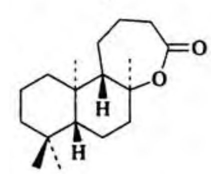
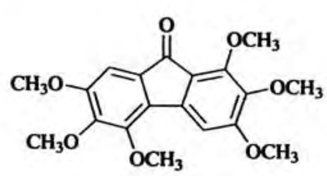
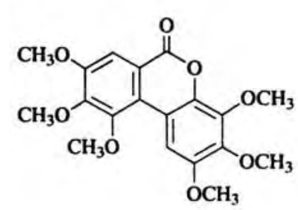
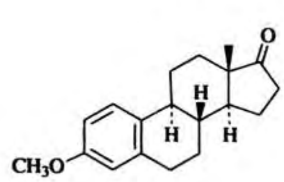
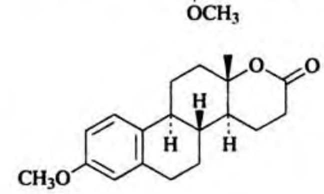
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, TsOH, CH_2Cl_2, 3.5 h, 25°	 (25)	888
	PBA, $CHCl_3$, 3–7 d, 30°	 (70–90)	268
	PBA, $CHCl_3$, 3–7 d, 30°	 (70–90)	268
	PBA, $CHCl_3$, 3–7 d, 30°	 (70–90)	268
	PBA, $CHCl_3$, 3–7 d, 30°	 (70–90)	268
	PBA	 (61)	999
C_{19}			
	MCPBA, H_2SO_4, CH_2Cl_2, 4 d, 0°	 (13)	320
	$C_6H_5SeO_3H$, Na_2HPO_4, THF, 24 h	 (80)	222
	30% H_2O_2, $C_6H_5AsO_3H_2$, $CHCl_3$, 48 h, 80°	" (80) (20)*	181, 182

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

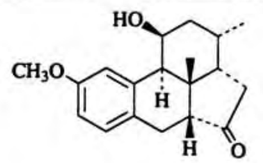
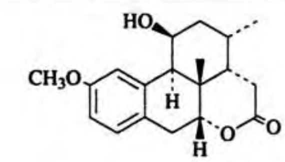
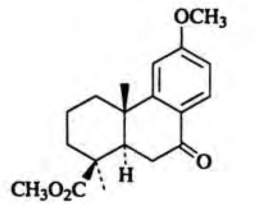
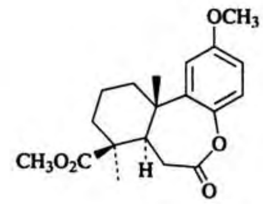
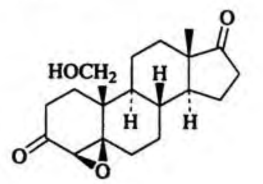
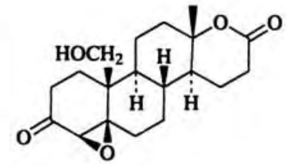
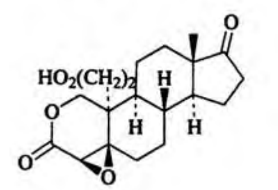
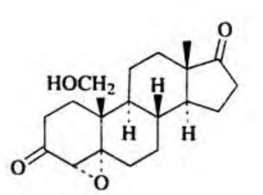
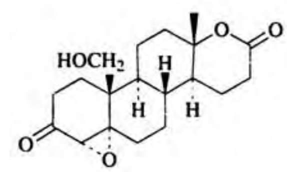
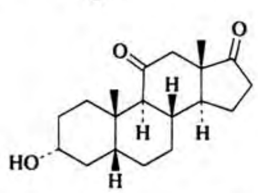
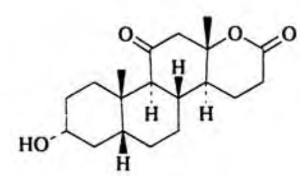
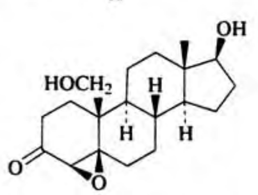
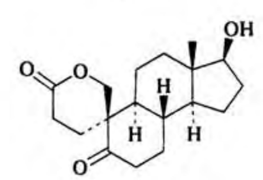
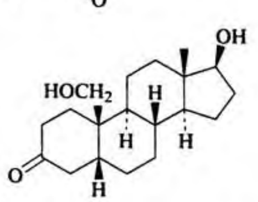
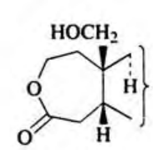
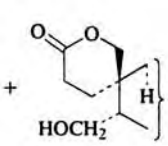
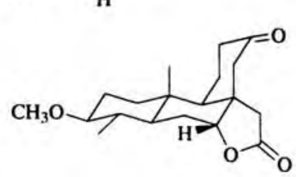
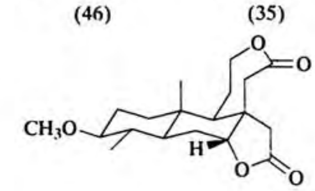
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, TsOH, CH_2Cl_2, 14 h, 25°		(24)	255, 256
	MCPBA, $CHCl_3$, 5 d, 25°		(88)	116
	MCPBA, $CHCl_3$, 4 d, 25°		(60) (27)*	1000
	1. 30% H_2O_2, NaOH, CH_3OH, 16 h, 0–25° 2. acidification		(85) (3)*	1088
	MCPBA, $CHCl_3$, 6 d, 25°		(20) (24)*	1000
	PBA, C_6H_6, 48 h, 25°		(75)	280
	MCPBA, $CHCl_3$, 11 d, 25°		(21)	1000
	MCPBA, $CHCl_3$, 2 d, 25°	 (46) +  (35)		1000
	MCPBA, $NaHCO_3$, CH_2Cl_2, 18 h, 25°		(77)	270

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

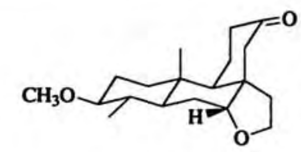
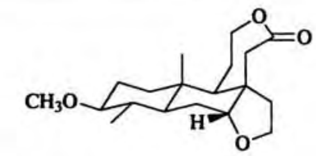
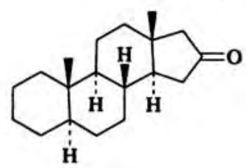
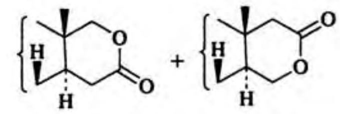
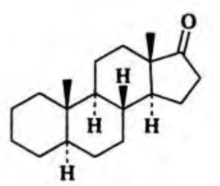
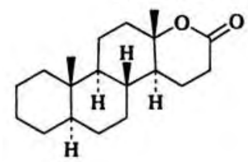
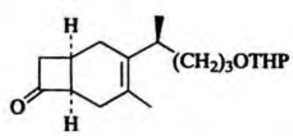
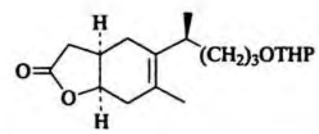
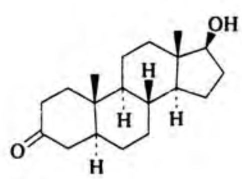
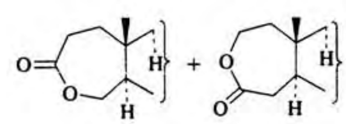
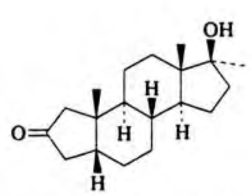
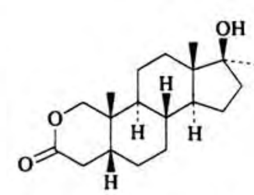
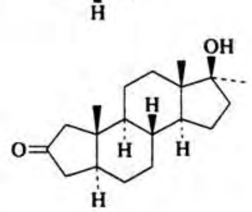
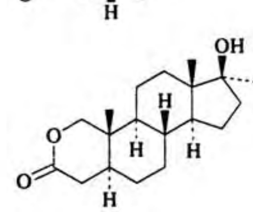
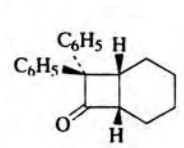
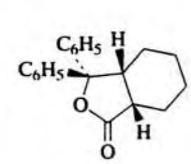
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°		(66)	270
	MCPBA, TsOH, CH_2Cl_2	 I II; I:II = 90:10	(80)	275
	MCPBA, TsOH, CH_2Cl_2, 5 h, 25°		(85)	275
	t-BuO_2H, NaOH, THF, 30 min, 0°		(76)	272, 1001
	MCPBA, $CHCl_3$, 2.5 d, 25°	 I II; I:II = 58:42	(85)	241, 1002
	TFPAA, Na_2HPO_4, CH_2Cl_2, 90 min, 25°	I:II = 100:0	(33)	1002
	PBA, $CHCl_3$, 3–7 d, 30°		(high)	268
	PBA, $CHCl_3$, 3–7 d, 30°		(70–90)	268
C_{20}				
	30% H_2O_2, NaOH, CH_3OH, 4 h, 25°		(94)	152

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

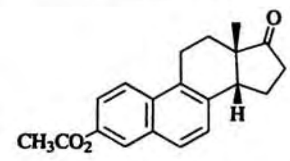
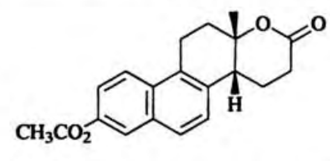
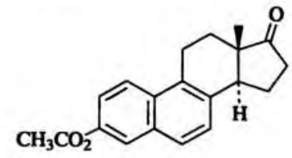
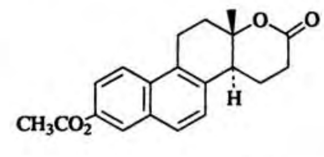
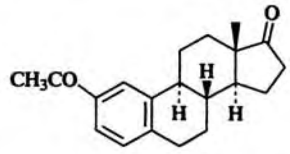
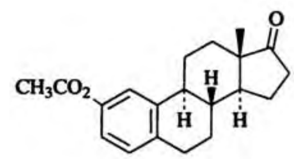
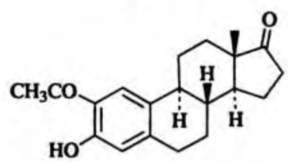
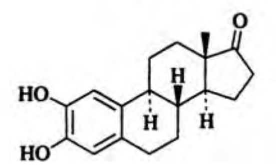
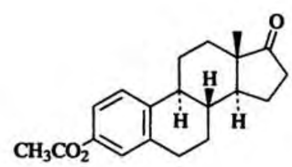
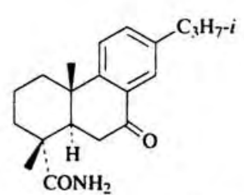
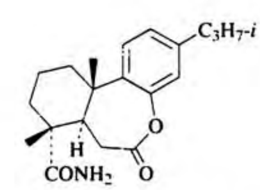
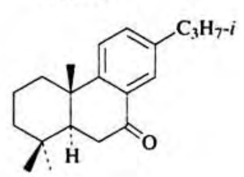
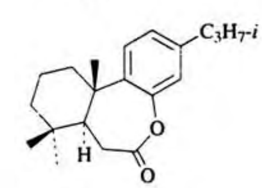
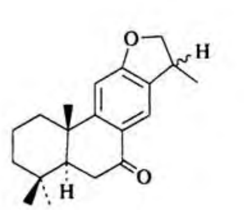
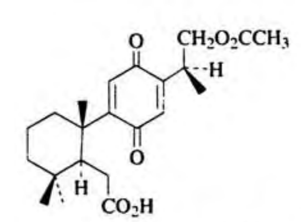
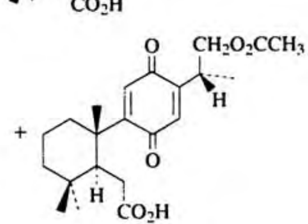
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, TsOH, AcOH, 12 h, 10°		(75)	1003
	PAA, TsOH, AcOH, 100 h, 10°		(84)	715, 1003
	PBA, $CHCl_3$, 7 d, 25°		(68)	118
	3% H_2O_2, NaOH (pH 8.2–8.5), 5 h, 12°		(93)	119
	PAA, TsOH, AcOH, 10°		(0)	714, 715, 1003
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, >30 min, 5–7°		(73)	1004
	MCPBA, $CHCl_3$, 8 d, 25°		(75)	1005
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, heat	"	(51)	117
	H_2O_2, Ac_2O, H_2SO_4	 + 	(—)	1006

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

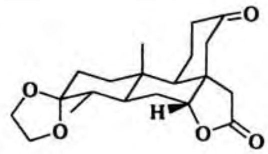
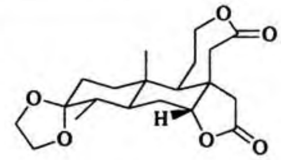
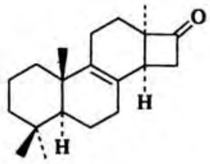
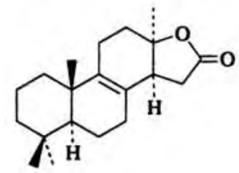
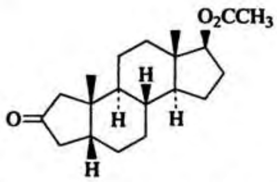
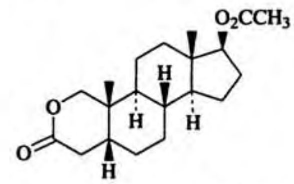
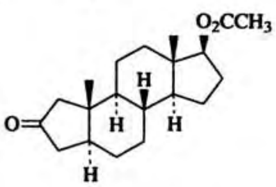
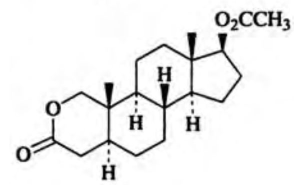
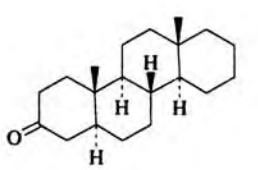
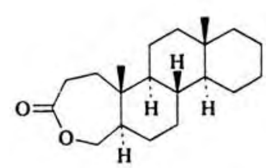
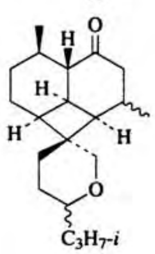
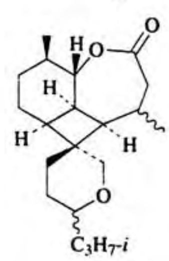
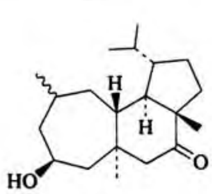
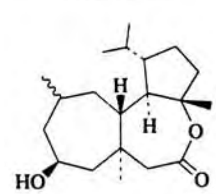
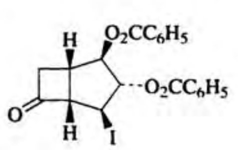
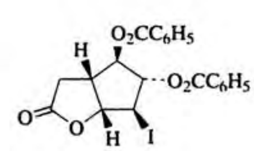
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h		(76)	270
	*t*-BuO_2H, NaOH, THF, 15 min, 0°		(59)	234
	PBA, $CHCl_3$, 5–7 d, 30°		(high)	268
	PBA, $CHCl_3$, 5–7 d, 30°		(70–90)	268
	PBA, $CHCl_3$, 12 h, 5°		(62)	1007
	MCPBA, TsOH, CH_2Cl_2, 48 h, 25°		(47)	892
	MCPBA, $CHCl_3$, 30 h, 25°		(63)	1008
C_{21}				
	1. 30% H_2O_2, 70% AcOH, 2 h, 0° 2. 3 h, 20°		(100)	245, 1009

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

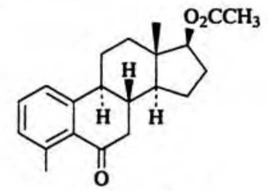
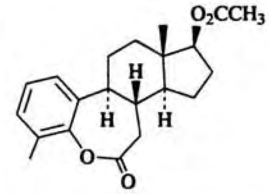
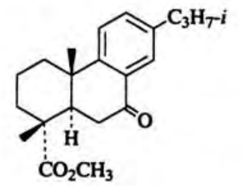
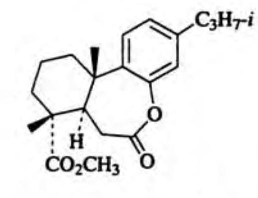
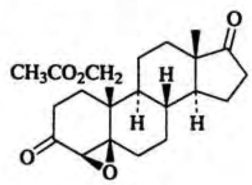
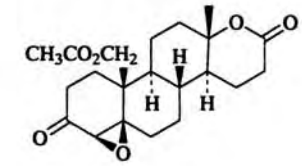
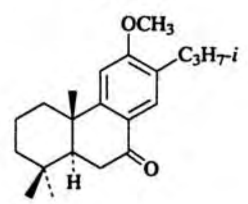
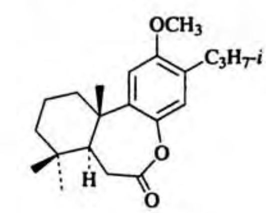
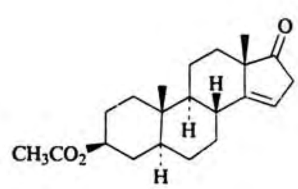
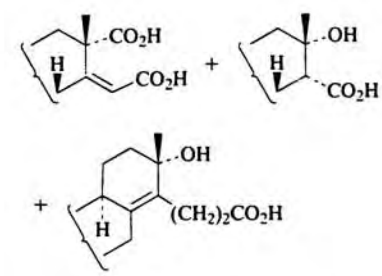
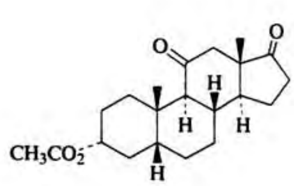
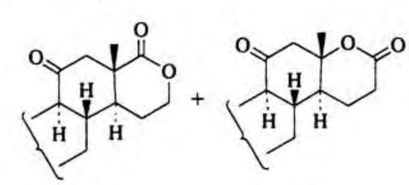
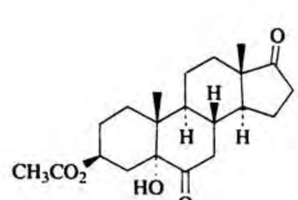
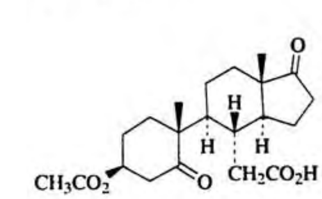
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2, 2 h, reflux	 (33)	1010
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 20 min, 25°	 (97)	998
	MCPBA, $CHCl_3$, 6 d, 25°	 (89) (4)*	1000
	MCPBA, $CHCl_3$, 8 d, 25°	 (96)	1005
	H_2O_2, NaOH, CH_3OH	 (85)	1011
	PBA, TsOH, AcOH, $CHCl_3$, 2 d, 20°	 I (26) II (38)	274
	PAA, AcOH, 24 h, 25°	I:II = 0:100 (77)	280, 714, 715
	PBA, $CHCl_3$, 10 h, 25°	 (96)	295

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

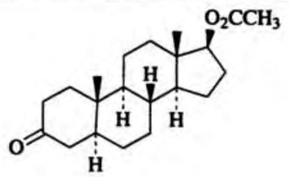
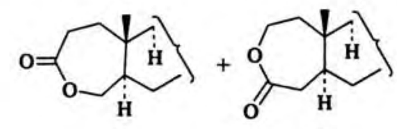
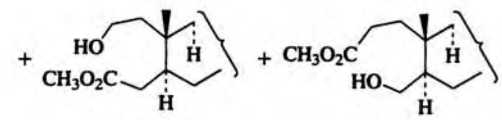
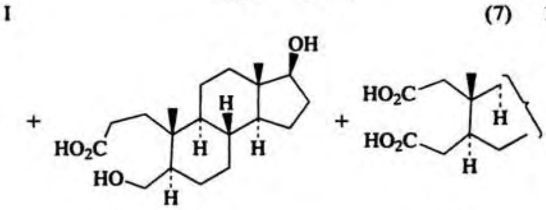
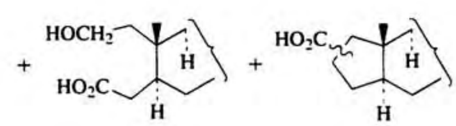
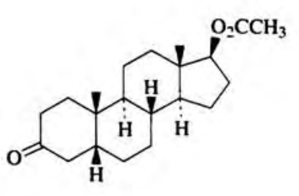
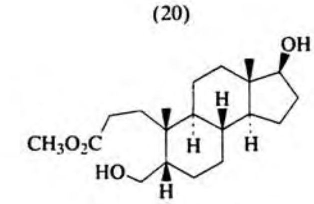
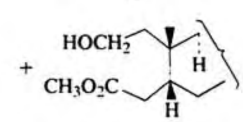
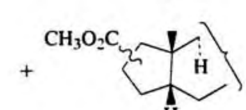
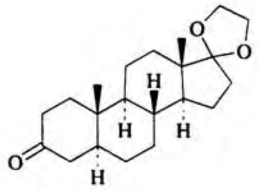
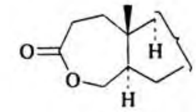
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 6 d, 0°	 I II; I:II = 55:45 (95)	240, 1012
	1. PBA, $CHCl_3$, 7 d, 0° 2. Lactone isolation 3. NaOH, CH_3OH 4. CH_2N_2	I (44)  III IV (—) III:IV = 50:50	1012
	1. 50% H_2O_2, SeO_2, *t*-BuOH, 7 h, reflux 2. Lactone isolation 3. NaOH, CH_3OH, 2 h, heat	I (7)  (25) (6)  (20) (23)	1012, 1013
	1. 50% H_2O_2, SeO_2, *t*-BuOH, 7 h, reflux 2. NaOH, CH_3OH 3. CH_2N_2	 (24)  (9)  (18)	1012, 1013
	MCPBA, $CHCl_3$, 16 h, 25°	 (—)	1014

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

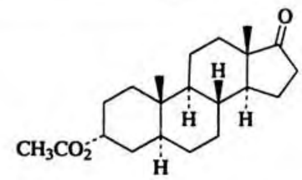
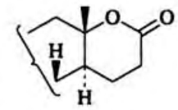
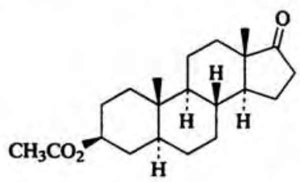
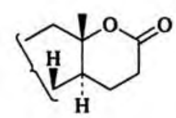
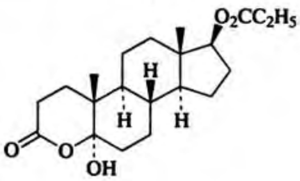
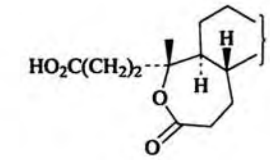
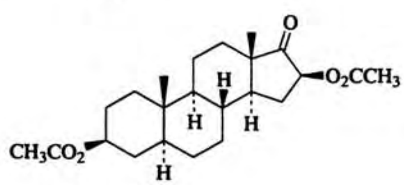
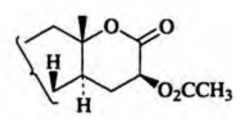
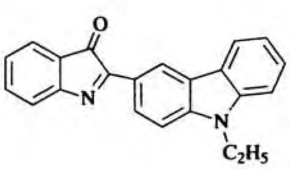
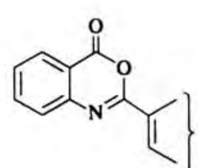
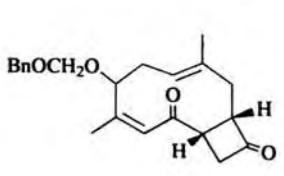
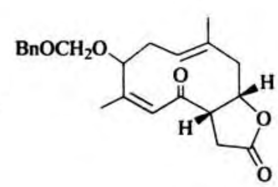
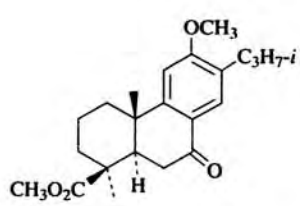
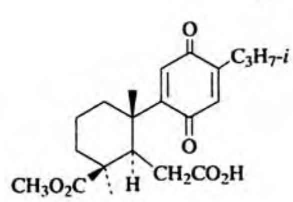
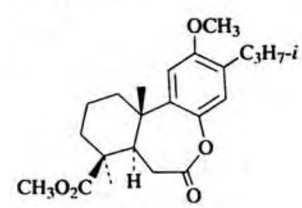
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	$[(CH_3)_3Si]_2O_2$, $(CH_3)_3SiOS(O)_2CF_3$, CH_2Cl_2, 20 h, −25 to −10°		(70) (19)*	221
	H_2O_2, SeO_2, *t*-BuOH, 7 h, 25°		(—)	370, 515
	50% H_2O_2, SeO_2, *t*-BuOH, 7 h, heat		(clean)	101
	40% PAA, TsOH, AcOH, 24 h, 25°		(97)	293
	35% H_2O_2, DMF, 15 h, 25°		(53)	644
	H_2O_2 (anh), Ti(OPr-*i*)$_4$, ether, (*i*-Pr)$_2$NC$_2$H$_5$, 15 min, −30°		(55)	236
	H_2O_2, Ac_2O, H_2SO_4, 7 h, 25°		(—)	1015
	MCPBA, $CHCl_3$, 4 d, 25°		(—)	1015

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

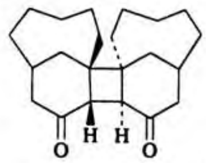
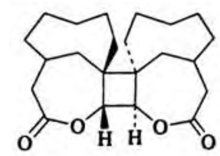
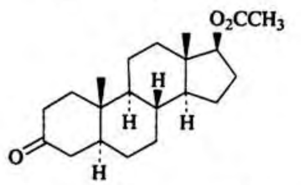
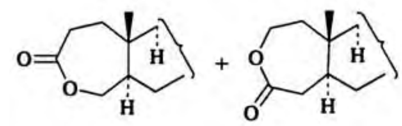
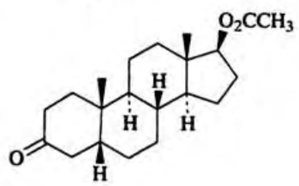
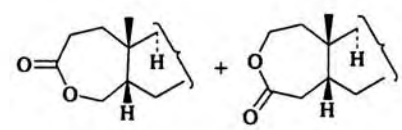
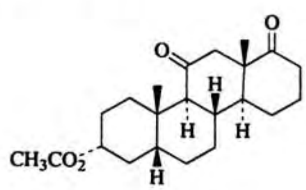
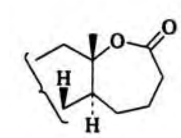
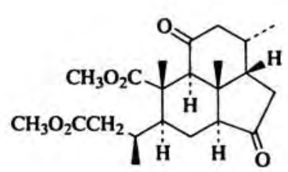
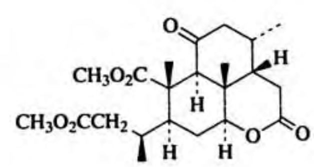
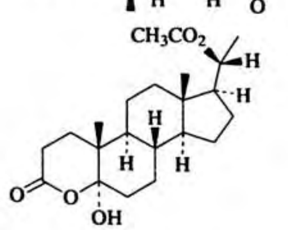
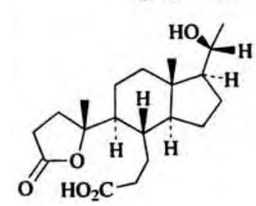
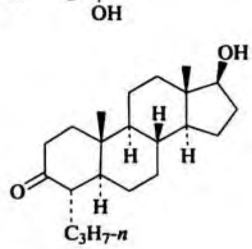
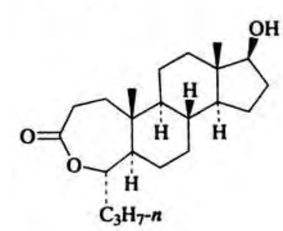
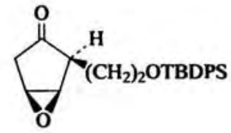
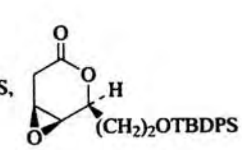
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	90% MCPBA, CH_2Cl_2, 18 d, 25°	 (94)	1016
	PBA, $CHCl_3$, 16 h, 25°	 (—)	1017
	PBA, $CHCl_3$, 16 h, 25°	 (—)	1017
C_{22}			
	PBA, benzene, 3 d, 25°	 (85)	280
	40% PAA, NaOAc, AcOH, 8 h, 65°	 (>75)	1018
	H_2O_2, AcOH	 (—)	101, 515
	55% MCPBA, CH_2Cl_2, 2 h, 25°	 (>63)	276
C_{23}			
	85% MCPBA, $NaHCO_3$, (3-*t*-Bu-4-OH-5-$CH_3C_6H_2)_2S$, CH_2Cl_2, 24 h, heat	 (>74)	160

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

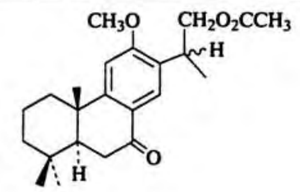
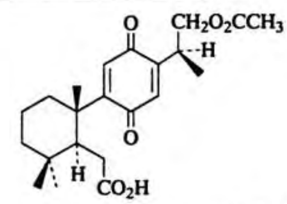
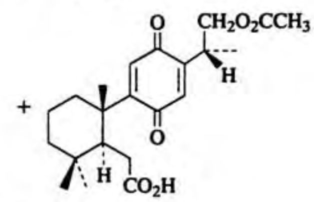
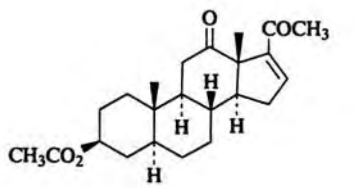
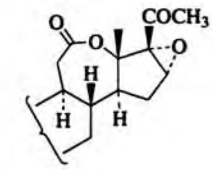
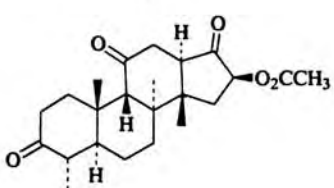
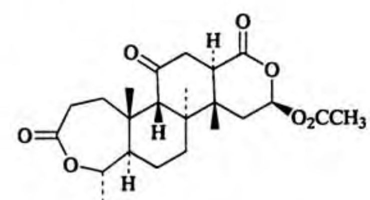
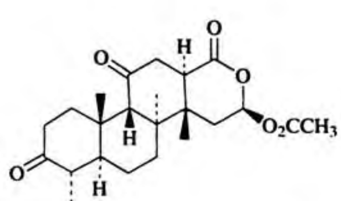
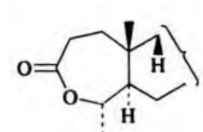
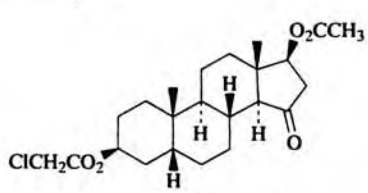
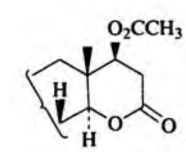
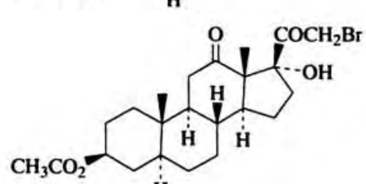
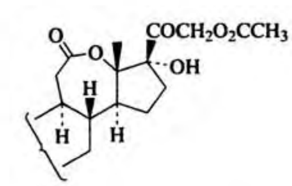
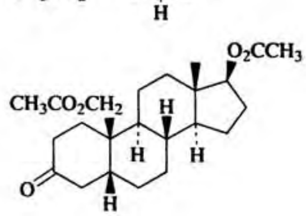
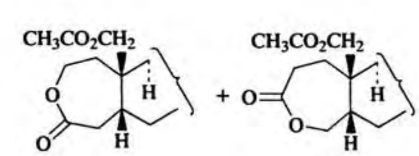
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, Ac_2O, H_2SO_4	 +  (—)	1006
	PBA, H_2SO_4, AcOH, $CHCl_3$, 14 d, 25°	 (16)	518
	MCPBA, CH_2Cl_2, 65 h, 25°	 (58)	292
	MCPBA, CH_2Cl_2, 65 h, 25°	 (41)	292
	1. MCPBA, $NaHCO_3$, CH_2Cl_2, 16 h, 25° 2. 2 h, heat	 (85)	1019
	PBA, H_2SO_4, AcOH, $CHCl_3$, 92 h, 25°	 (36)	282
	MCPBA, $CHCl_3$, 2 d, 25°	 (32) + (32)	1000

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

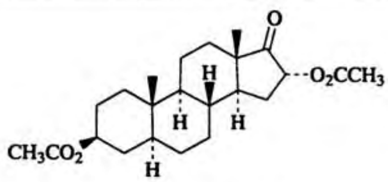
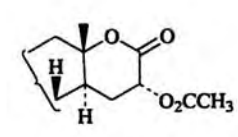
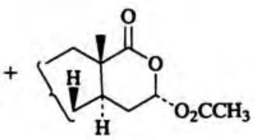
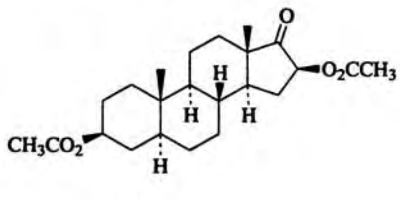
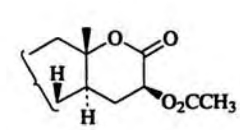
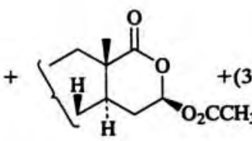
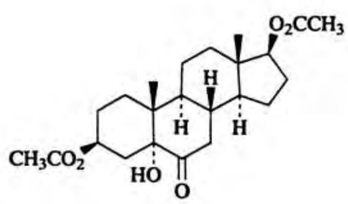
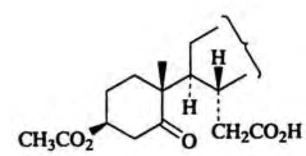
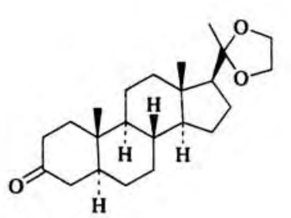
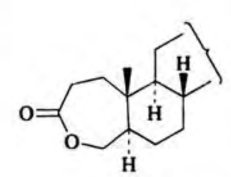
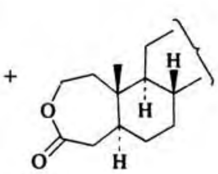
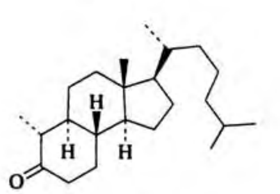
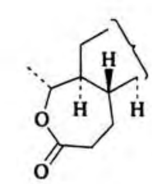
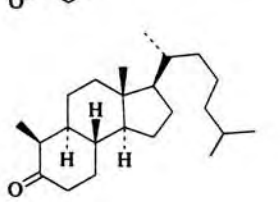
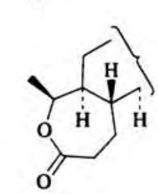
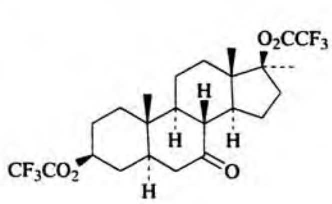
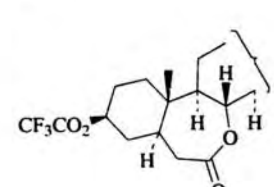
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 48 h, 40°	 (8) +  (4)	289
	MCPBA, $CHCl_3$, 48 h, 40°	 I (36) +  II (9) +(30)*	289
	40% PAA, TsOH, AcOH 24 h, 25°	I (97)	293
	PBA, $CHCl_3$, 24 h, 25°	 (80)	296
	40% PAA, $CHCl_3$, 18 h, 40°	 I +  II (82) I:II = 50:50	1020
	MCPBA, $CHCl_3$, 3 d, 25°	 (66)	1021
	MCPBA, $CHCl_3$, 24 h, 25°	 (79)	1021
C_{24}			
	MCPBA, $CHCl_3$, 4 h, reflux	 (99)	903

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

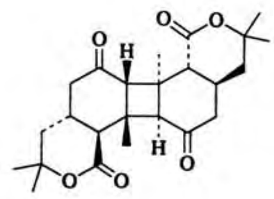
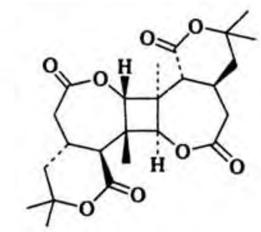
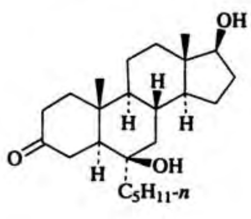
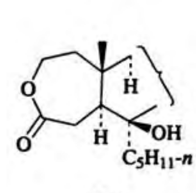
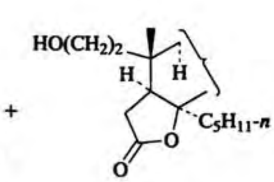
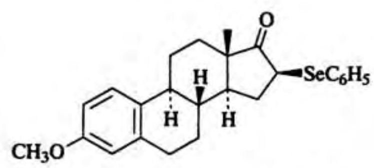
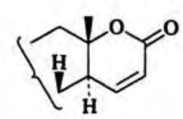
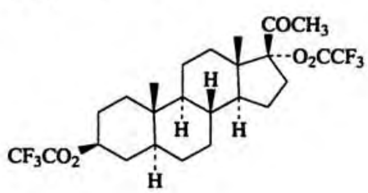
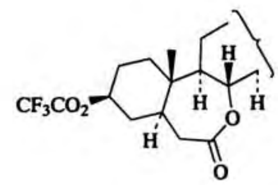
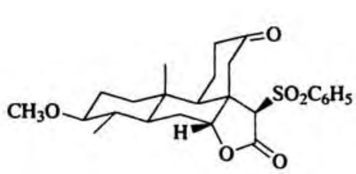
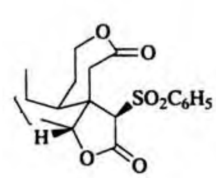
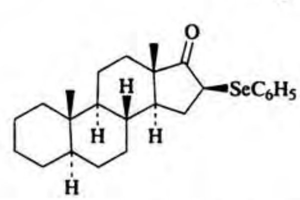
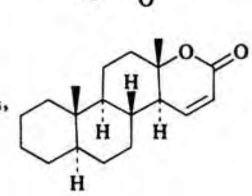
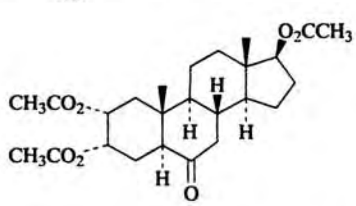
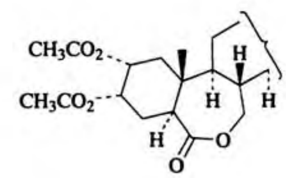
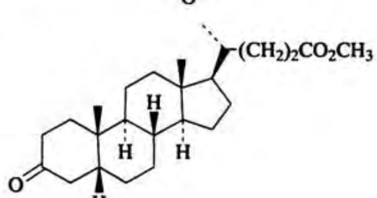
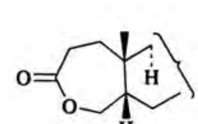
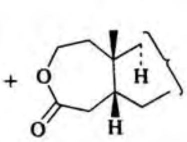
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (90%), CH_2Cl_2, 1 h, 0°	 (—)	1022
	70% MCPBA, CH_2Cl_2, 3.5 h, 25°	 (51) +  (25)	659
C_{25}			
	30% H_2O_2, CH_2Cl_2–CH_3OH, 2.5 h, 25°	 (66)	109
	87% MCPBA, $CHCl_3$, 64 h, 25°	 (70)	279
	MCPBA, BF_3 etherate, 12 h, 25°	 (88)	270
	30% H_2O_2, THF–$CH_3CO_2C_2H_5$, 1 h, 0°	 (50)	302
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, heat	 (41)	1023
	PBA, $CHCl_3$, 16 h, 18°	 +  (—)	1017

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

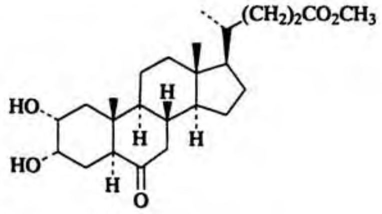
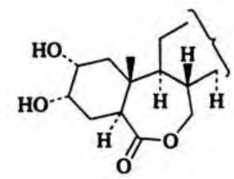
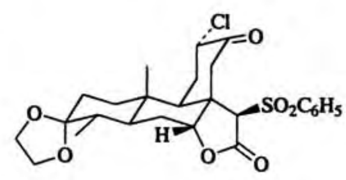
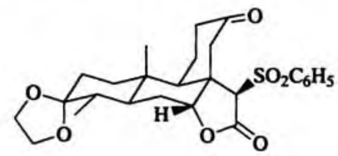
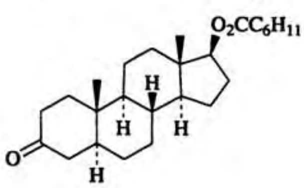
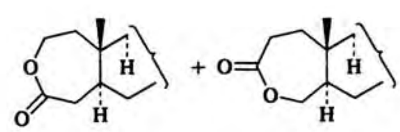
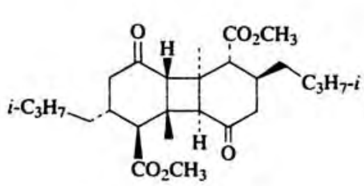
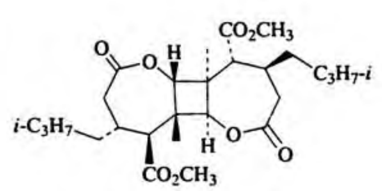
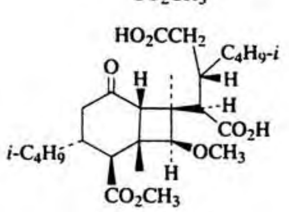
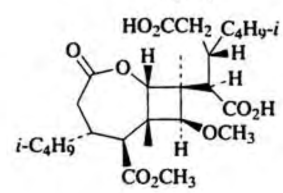
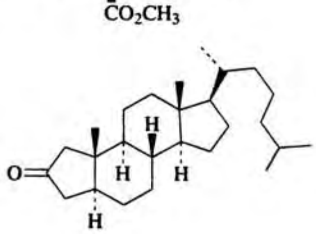
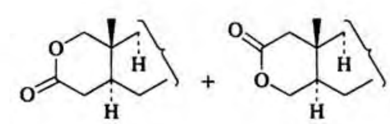
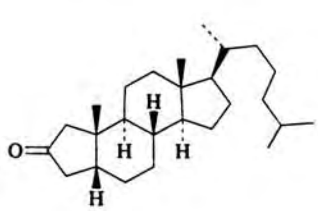
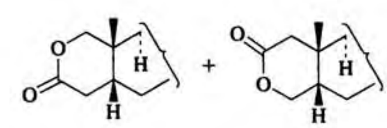
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, CH_2Cl_2		(86)	1024
C_{26}				
	MCPBA, TFPAA, or DNPBA, CH_2Cl_2, heat		(0)	270
	MCPBA, TFPAA, or DNPBA, CH_2Cl_2, heat		(0)	270
	TFPAA (85%), Na_2HPO_4, CH_2Cl_2, 10 min, 0°	 (6) (30)		1025
	TFPAA (90%), CH_2Cl_2, 1 h, 0°		(52)	1022
	TFPAA (90%), CH_2Cl_2, 1 h, 0°		(—)	1022
	TFPAA, Na_2HPO_4, $CHCl_3$, 24 h, 25°	 I II I:II = 70:30	(88)	266, 267, 268
	75% MCPBA, $CHCl_3$, 24 h, 25°	I:II = 80:20	(96)	267
	75% MCPBA, $CHCl_3$, 43 h, 25°	 I II I:II = 79:21	(96)	267, 268

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

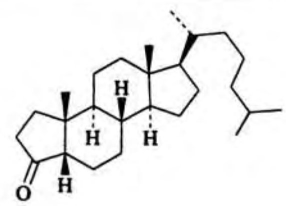
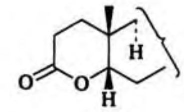
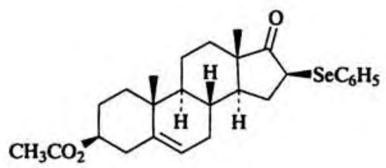
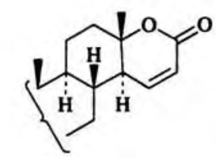
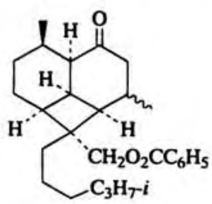
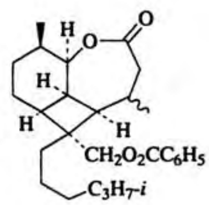
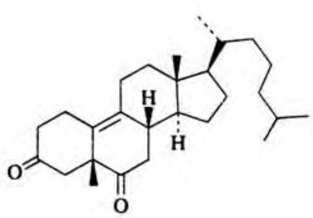
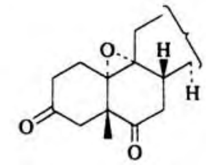
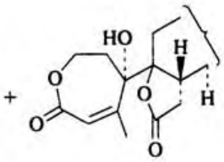
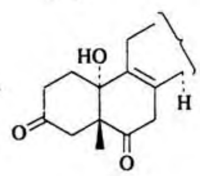
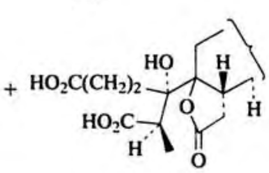
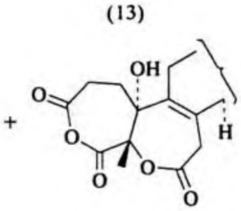
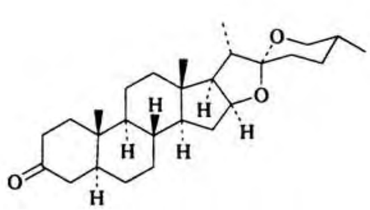
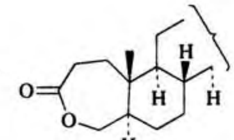
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PAA, TsOH, AcOH, 24 h, 35°	 (90)	253
C_{27}			
	30% H_2O_2, CH_2OH, CH_2Cl_2, 1 h	 (95)	109
	MCPBA, TsOH, $CHCl_3$, 48 h, 25°	 (79)	892
	PBA, TsOH, $CHCl_3$, 3 d, 25°	 (18) +  (6) +  (13) +  (6) +  (7)	1026
	PBA, $HClO_4$, $CHCl_3$, 48 h, 25°	 (54)	1027, 1028

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

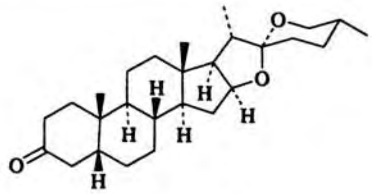
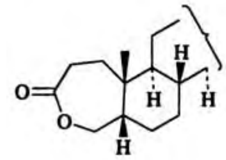
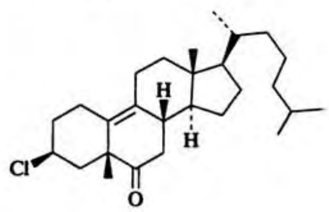
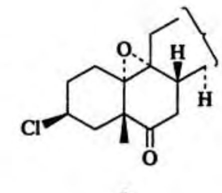
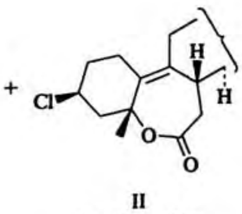
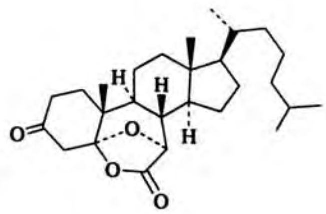
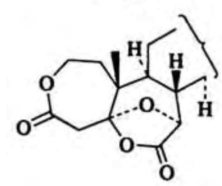
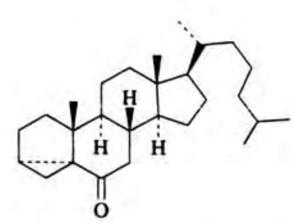
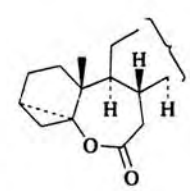
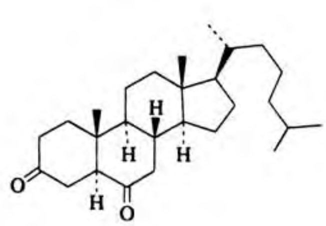
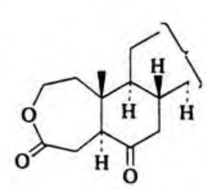
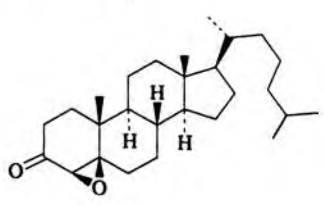
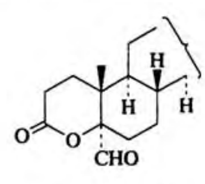
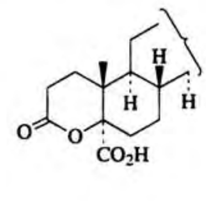
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, $HClO_4$, $CHCl_3$, 48 h, 25°	 (53)	1027
	PBA, TsOH, $CHCl_3$, 3 d, 25°	 I +  II; I = (36), I + II = (23)	1026
	PBA, TsOH, $CHCl_3$, 60 h, 25°	 (58)	303
	MCPBA, TsOH, CH_2Cl_2, 12 h, 25°	 (83)	275
	PBA, TsOH, $CHCl_3$, 3 d, 25°	" (43)	277
	PBA, TsOH, $CHCl_3$, 48 h, 25°	 (63)	278
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h, 25°	 (29)	509
	30% H_2O_2, NaOH, CH_3OH, 24 h, reflux	 (83)	297

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

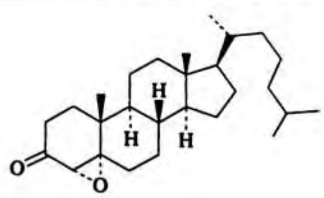
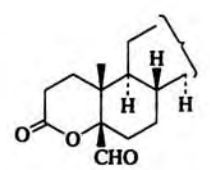
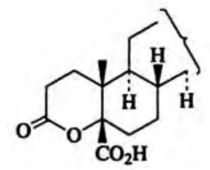
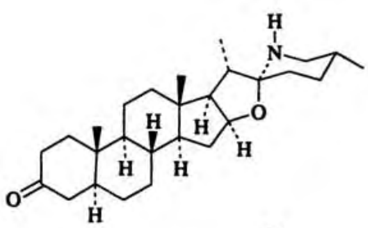
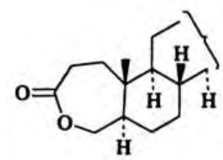
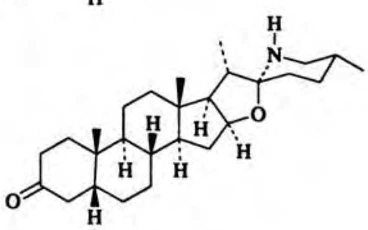
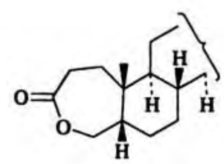
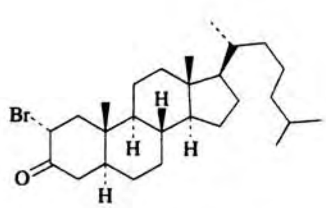
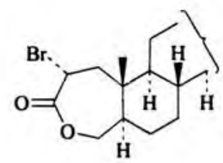
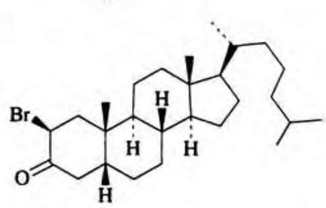
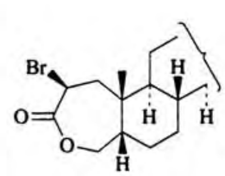
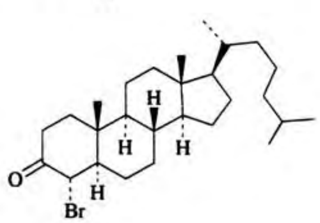
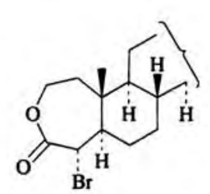
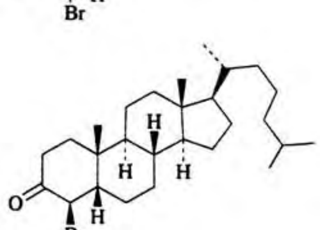
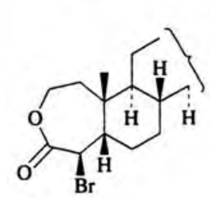
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h, 25°	 (4)	509
	30% H_2O_2, NaOH, CH_3OH, 24 h, reflux	 (75)	297
	PBA, $HClO_4$, $CHCl_3$, 48 h, 25°	 (52)	1029
	PBA, $HClO_4$, $CHCl_3$, 48 h, 25°	 (48)	1029
	MCPBA, $CHCl_3$, 12 h, 25°	 (100)	241, 266, 286
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 (92)	240
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 (80)	240
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 (53)	240

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

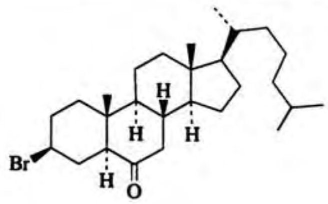
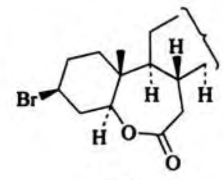
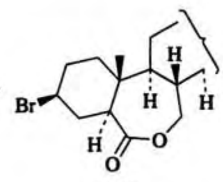
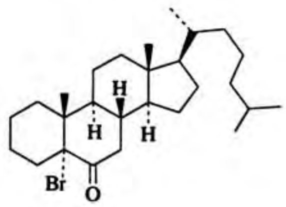
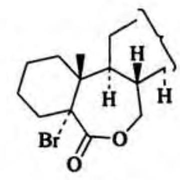
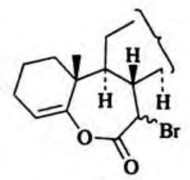
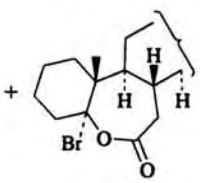
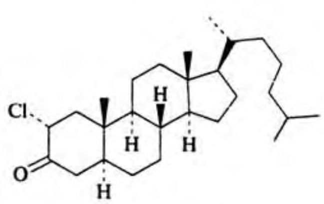
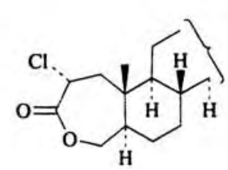
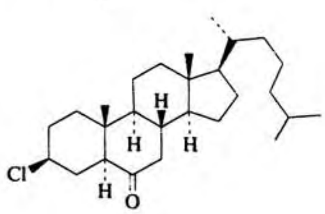
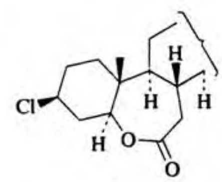
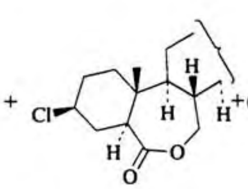
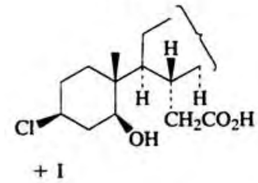
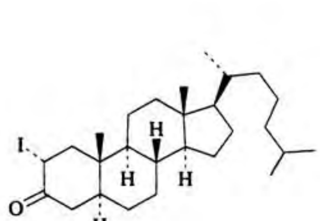
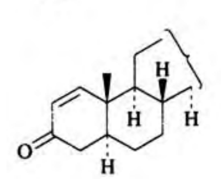
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 (18) +  (22) (31)*	277, 306, 307
	PBA, TsOH, $CHCl_3$, 4 d, 25°	 (9) +  (8) (6)* +  (8)	287
	TFPAA, Na_2HPO_4, $CHCl_3$, 80 min, 30–40°	 (—)	266
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 I (17) +  II (17) +(27)*	306
	PBA, TsOH, $CHCl_3$, 96 h, 25°	 (4) + I (19)	277
	TFPAA, Na_2HPO_4, $CHCl_3$, 2 h, reflux	 (41)	266

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

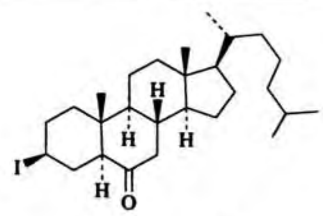
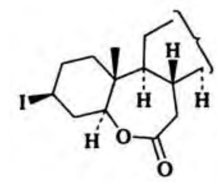
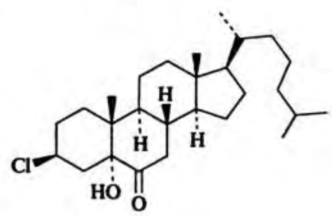
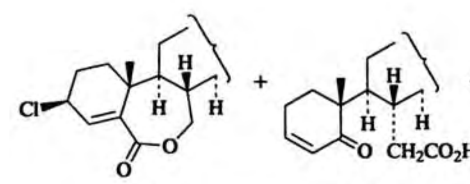
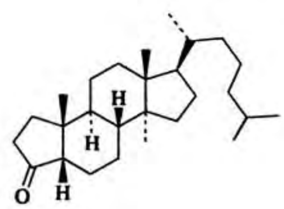
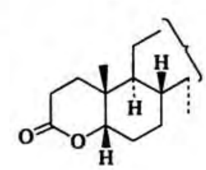
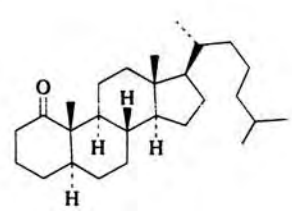
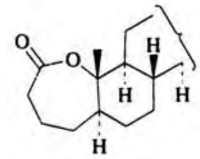
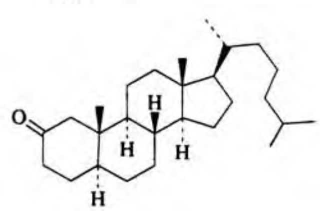
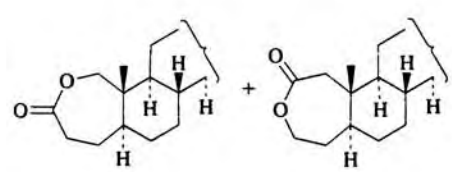
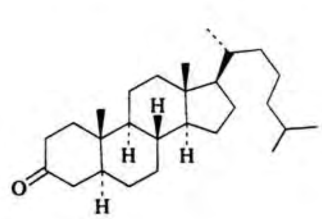
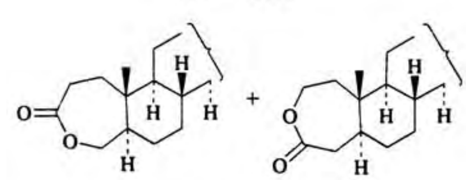
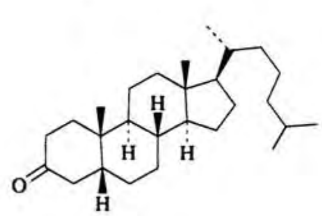
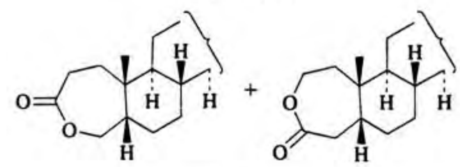
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 96 h, 25°	 (19)	306
	PBA, TsOH, $CHCl_3$, 40 h, 25°	 +(20)* (40) (5)	288
	1. TFPAA (90%), CH_2Cl_2, 24 h, 0° 2. 2 min, reflux	 (78)	251, 252
	MCPBA, TsOH, CH_2Cl_2	 (—)	275
	75% MCPBA, $CHCl_3$, $CHCl_3$, 7 d, 25°	 (92) I II I:II = 75:25	267
	TFPAA (63%), Na_2HPO_4, CH_2Cl_2, 2 h, 25°	 (95) I II I:II = 58:42	241, 275, 914, 1002, 1017, 1030, 1031, 1032, 1033
	MCPBA, $CHCl_3$, 25°	 (88) I II I:II = 58:42	241, 1017

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

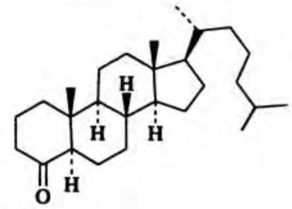
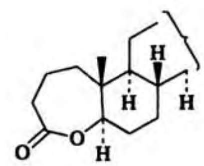
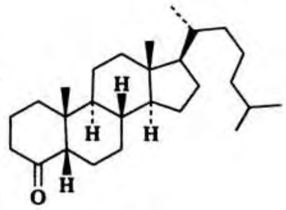
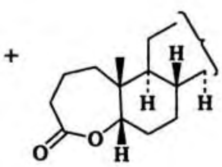
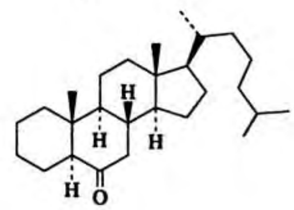
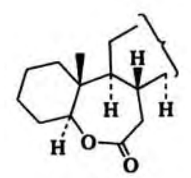
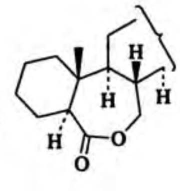
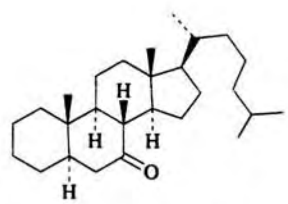
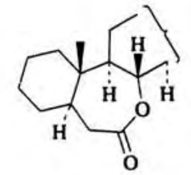
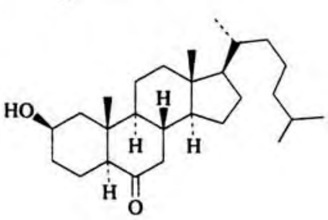
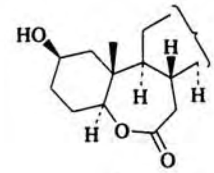
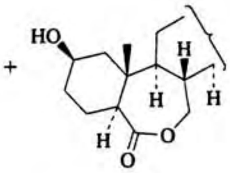
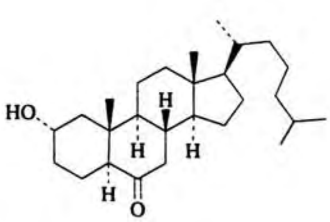
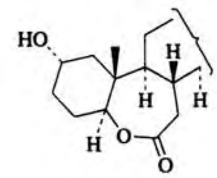
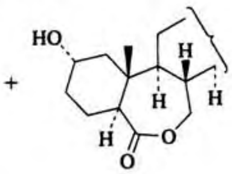
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 I	MCPBA, TsOH, CH_2Cl_2, 5 h, 25°	 II (63)	275, 1034
I + 	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1 h, 0° 2. 2 h, 20°	II +  (—)	1035
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 I (37) +  II (12) +(15)*	306, 309
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	I:II = 92:8 (100)	273
	MCPBA, TsOH, CH_2Cl_2	 (89)	275
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 35:65	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 22:78	273

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

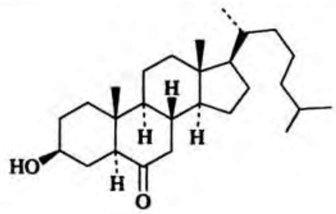
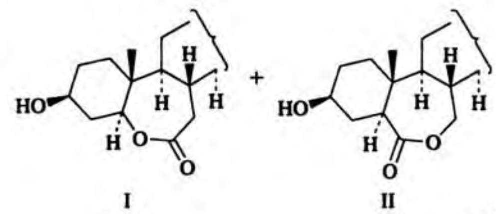
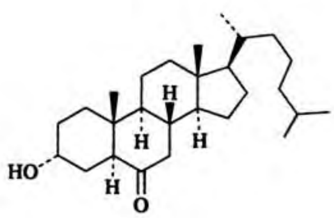
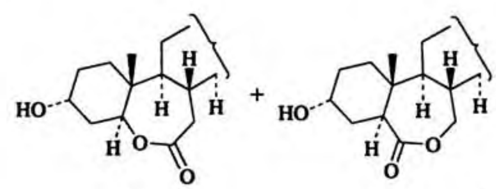
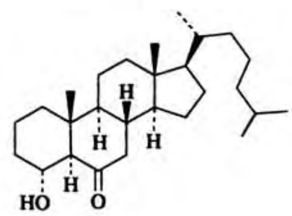
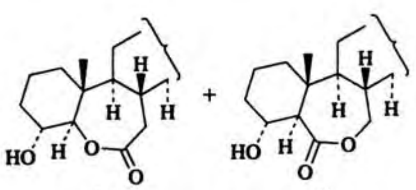
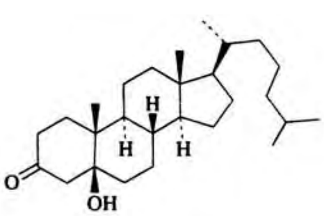
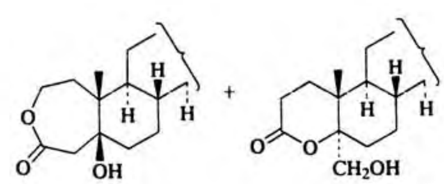
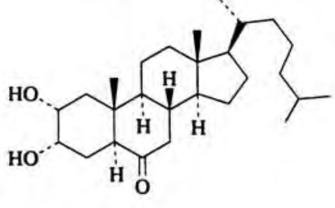
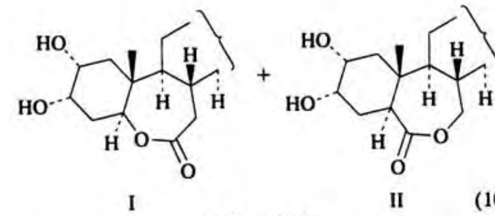
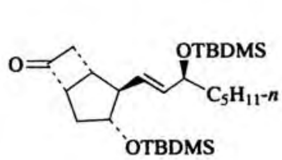
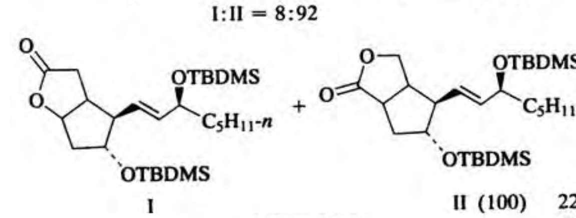
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 I (19) + II (19) +(17)*	306
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	I:II = 37:63 (100)	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 36:64	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 31:69	273
	TFPAA, Na_2HPO_4, $CHCl_3$, 12 h, 25°	 (20) + (40)	509
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 8:92	273
	PAA, NaOAc, CH_2Cl_2, 24 h, −20°	 I + II (100) I:II = 85:15	229, 728 994

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

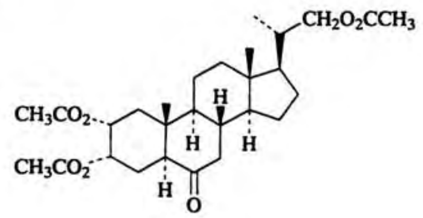
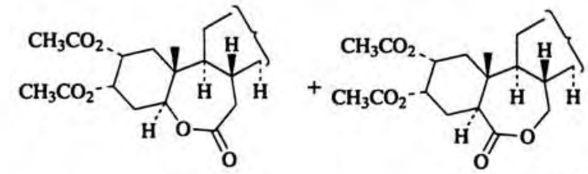
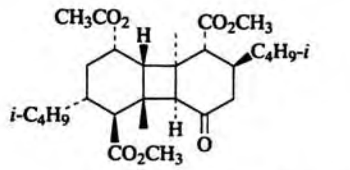
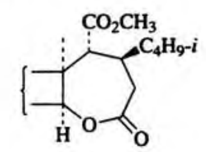
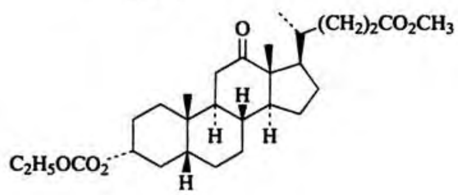
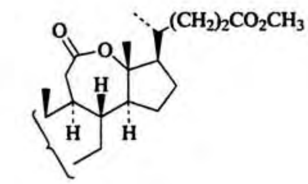
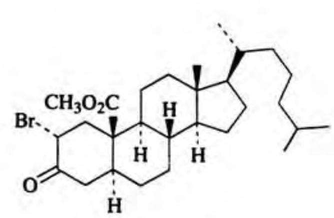
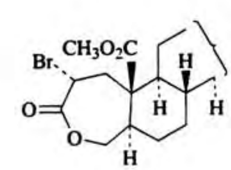
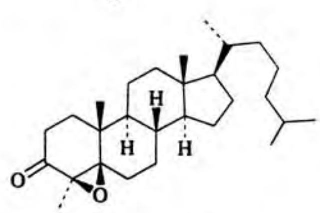
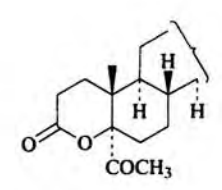
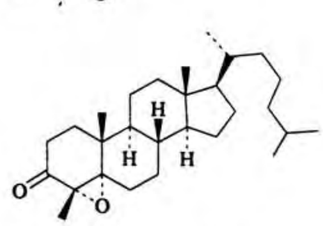
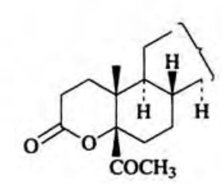
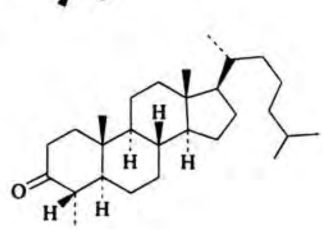
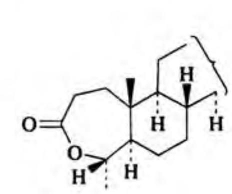
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{28}			
	TFPAA (30%), CH_2Cl_2	 I + II (—) I:II = 12:88	1036
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, 0°	I:II = 0:100 (83)	1023, 1037, 1038
	TFPAA (90%), CH_2Cl_2, 1 h, 0°	 (53)	1022
	PBA, H_2SO_4, AcOH, $CHCl_3$, 10 d, 25°	 (98)	1039
	MCPBA, $CHCl_3$, 12 h, 25°	 (65)	286
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h	 (31)	509
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h	 (48)	509
	MCPBA, $CHCl_3$, 18 h, 25°	 (82)	669, 1040

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

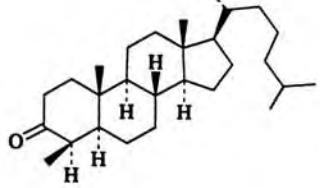
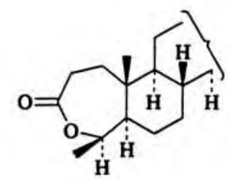
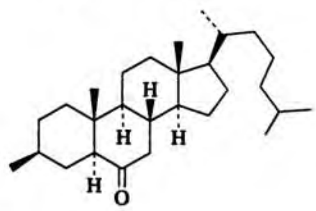
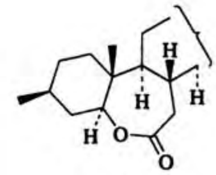
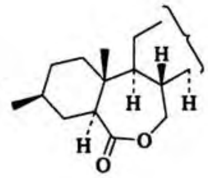
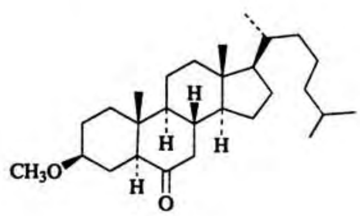
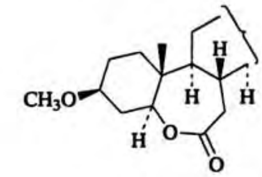
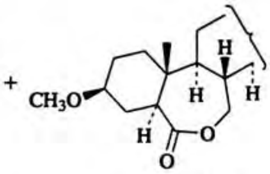
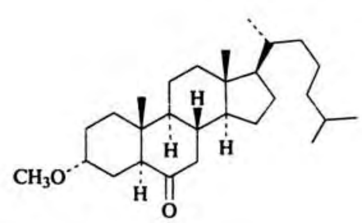
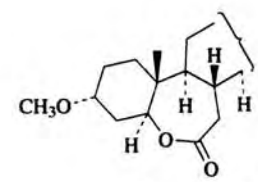
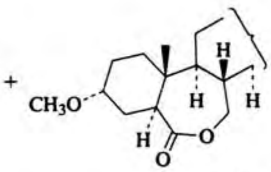
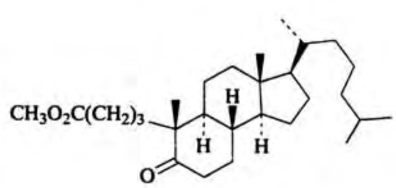
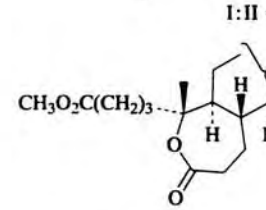
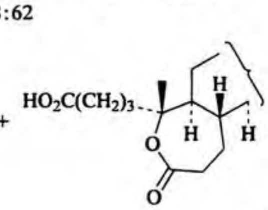
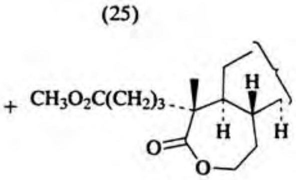
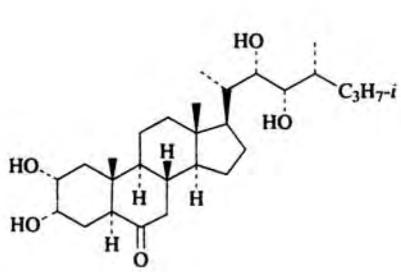
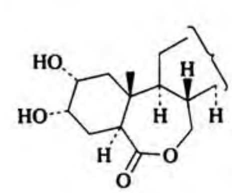
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 16 h, 32°	 (75)	1040
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 80:20	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 36:64	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 38:62	273
	PBA, $CHCl_3$, 96 h, 25°	 (25) +  (5) +  (4)	169
	TFPAA (30%), CH_2Cl_2, 3 h, 0°	 (80)	1041

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

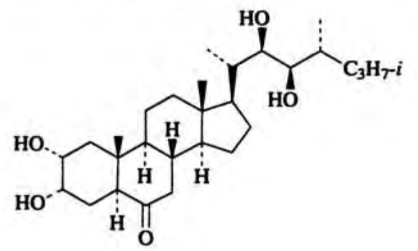
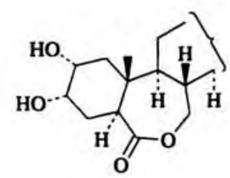
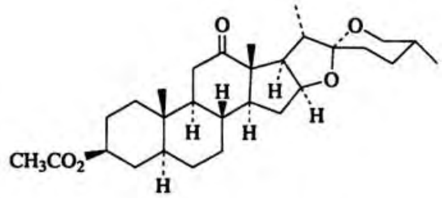
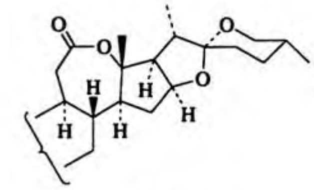
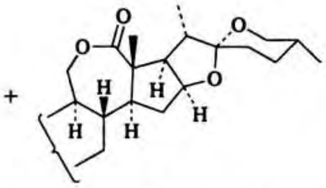
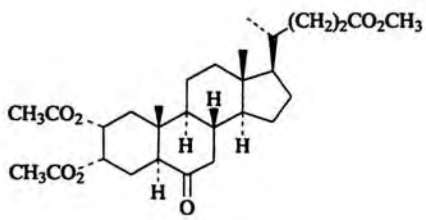
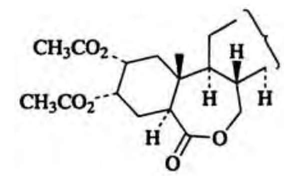
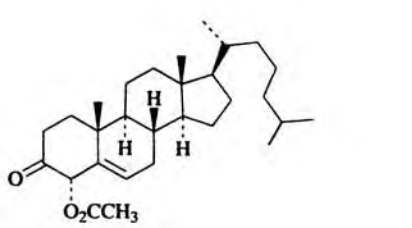
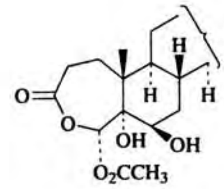
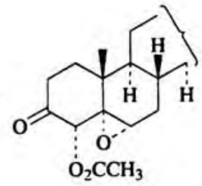
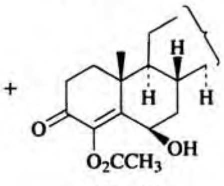
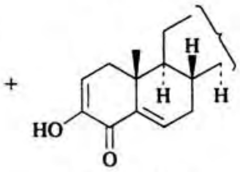
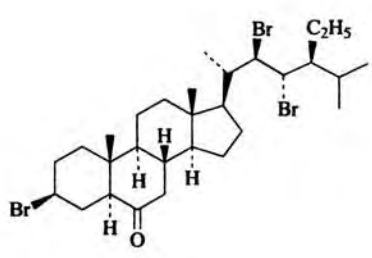
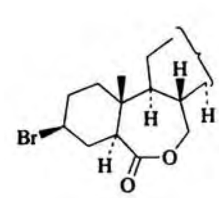
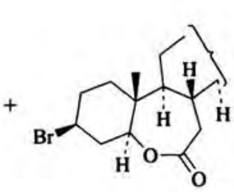
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (30%), CH_2Cl_2, 3 h, 0°	 (83)	1041
C_{29}			
	30% H_2O_2, H_2SO_4, AcOH–$CHCl_3$, 11 d, 25°	 I (82) +  II (5)	283
	PBA, H_2SO_4, AcOH, $CHCl_3$, 12 d, 25°	I (98)	1039
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 (99)	1024
	PBA (1 eq), TsOH, $CHCl_3$, 56 h, 25°	 I (<11) +  II (10) +  III (7) +  IV (3)	290
	PBA (2 eq), TsOH, $CHCl_3$, 144 h, 25°	I (54)	290
	TFPAA (30%), CH_2Cl_2, 6 h, heat	 (23) +  (20)	308

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

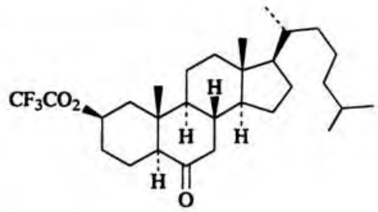
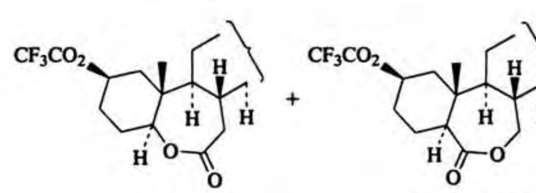
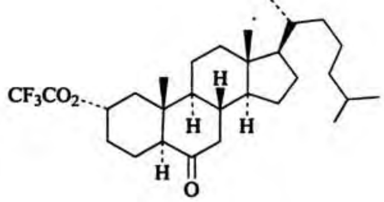
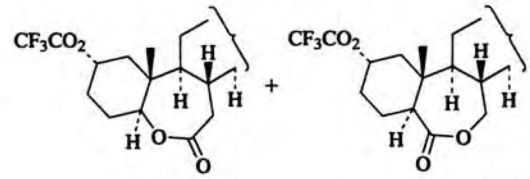
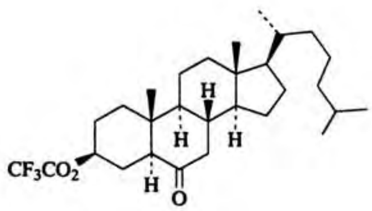
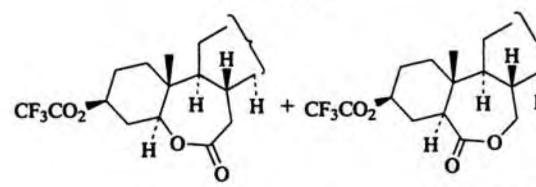
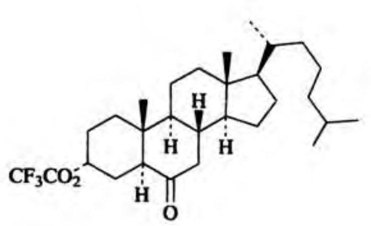
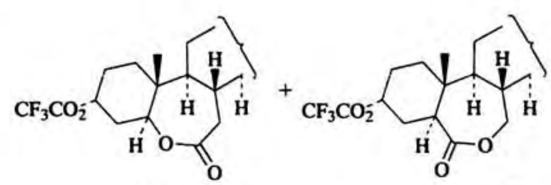
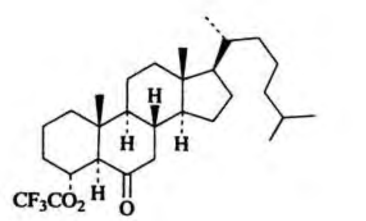
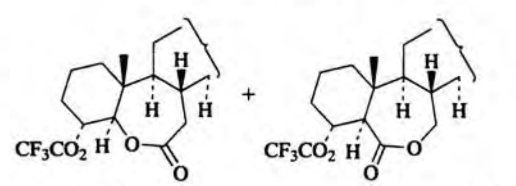
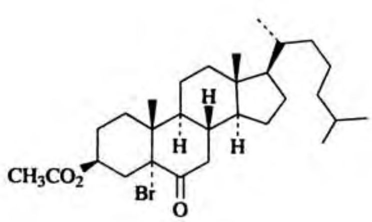
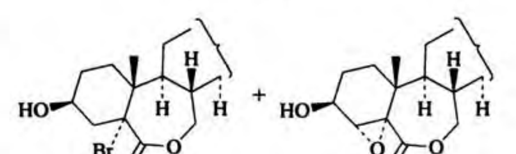
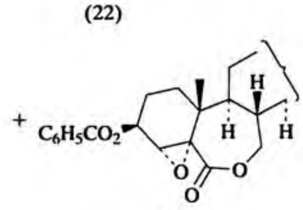
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 25:75	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 17:83	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 28:72	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 30:70	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 16:84	273
	PBA (2.5 eq), TsOH, $CHCl_3$, 4 d, 25°	 (22) + (14) +  (13)	287

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

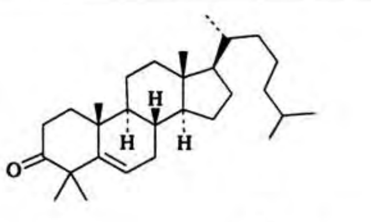
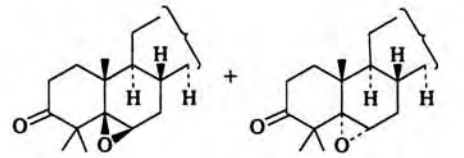
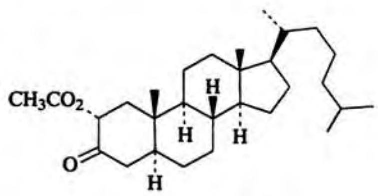
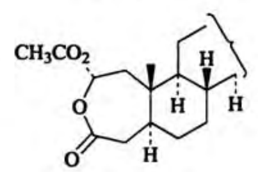
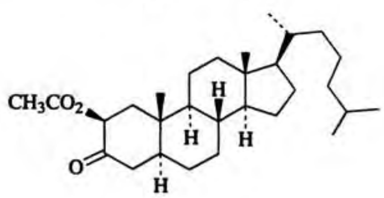
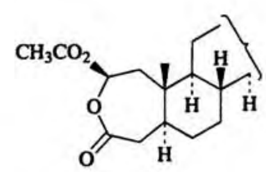
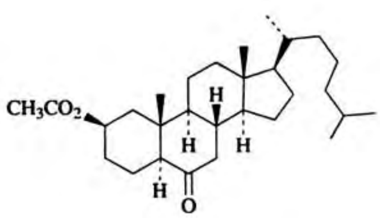
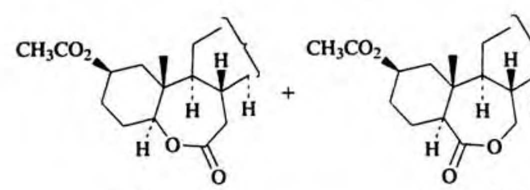
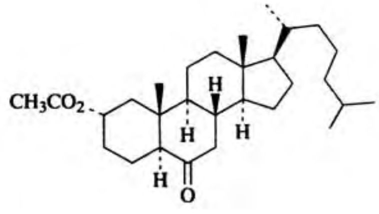
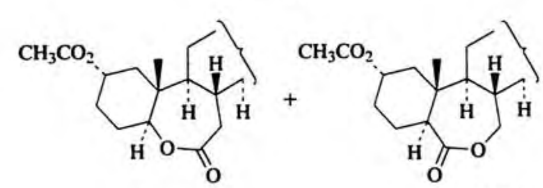
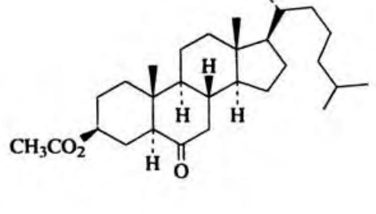
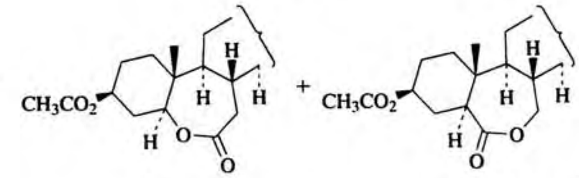
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 (15) + (10)	512
	MCPBA, $CHCl_3$, 12 h, 25°	 (93)	199, 289
	MCPBA, $CHCl_3$, 12 h, 25°	 (88)	289
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 30:70	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 30:70	273
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 I + II (46) (23)* I:II = 50:50	306, 309

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

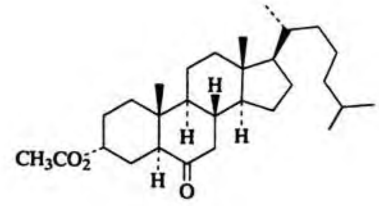
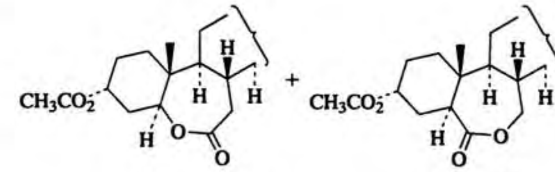
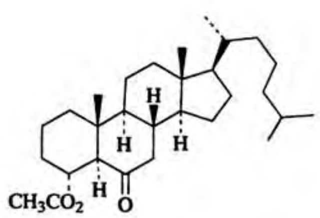
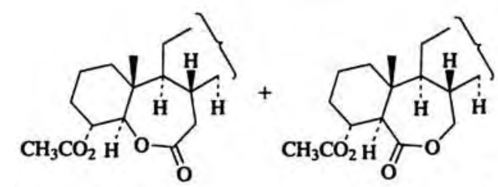
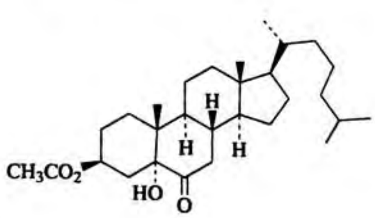
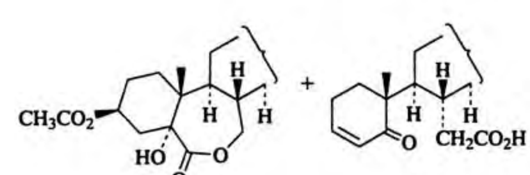
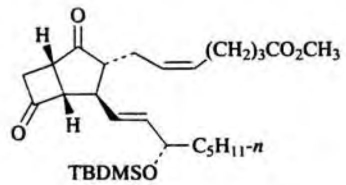
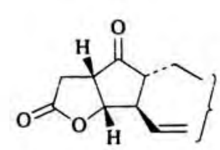
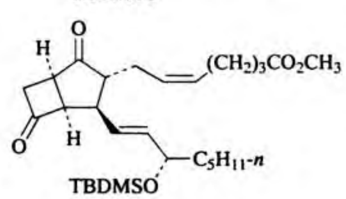
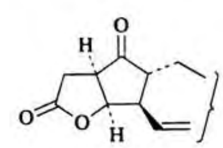
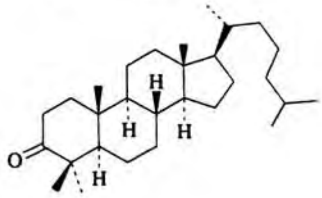
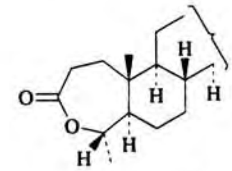
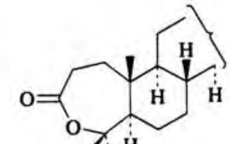
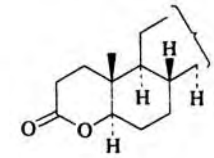
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, $CHCl_3$, 107 h, 25°	I:II = 24:76 (85)	309, 310
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	I:II = 28:72 (100)	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 40:60	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 25:75	273
	PBA, TsOH, $CHCl_3$, 40 h, 25°	 (19) + (11)	288
	30% H_2O_2, AcOH, 0°	 (90)	1042
	30% H_2O_2, AcOH, 0°	 (90)	1042
	MCPBA, H_2SO_4, AcOH, CH_2Cl_2, 90 h, 25°	 (65)	669, 670
	MCPBA, CH_2Cl_2–$CHCl_3$, 24 h, 25°	 (97)	669, 1040
	40% PAA, BF_3 etherate, CH_2Cl_2, 16 h, 6°	 (33)	284, 285

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

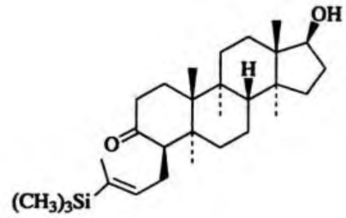
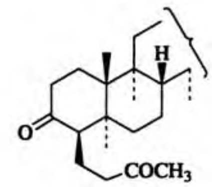
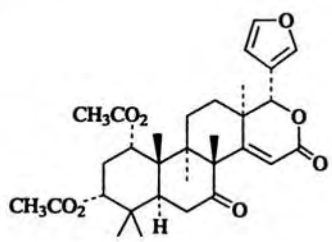
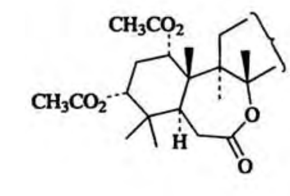
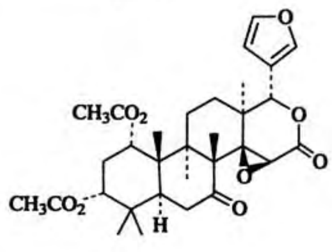
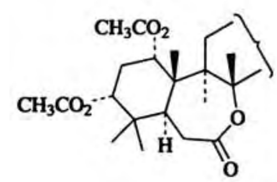
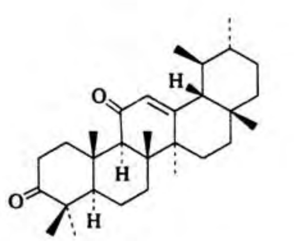
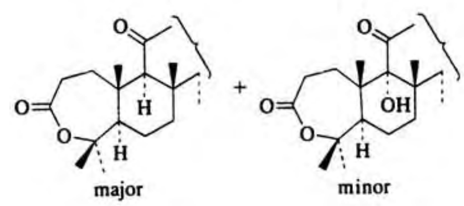
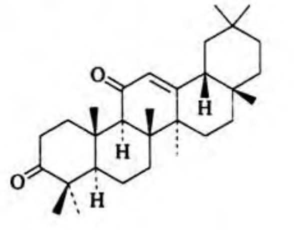
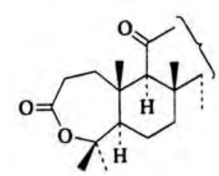
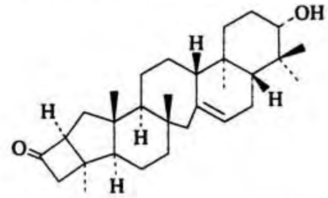
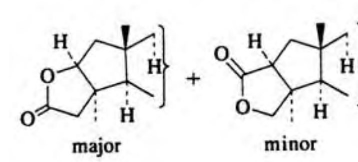
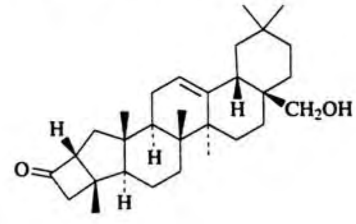
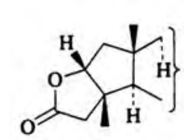
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2, 4 h, 25°	 (71)	217
C_{30}			
	PAA	 (—)	1043
	PAA	 (—)	1044
	PBA (1 eq), $CHCl_3$, 45 h, 25°	 (—)	502
	PBA, $CHCl_3$, 48 h, 5°	 (—)	502
	H_2O_2, NaOH, 0°	 (—)	656
	H_2O_2, NaOH, 0°	 (—)	656

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

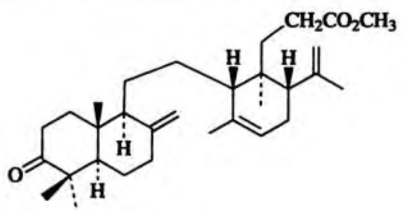
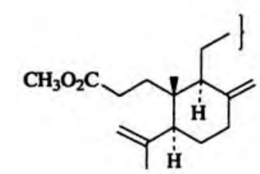
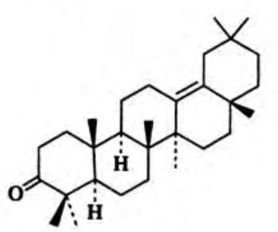
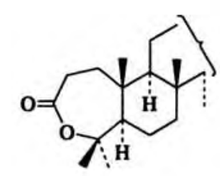
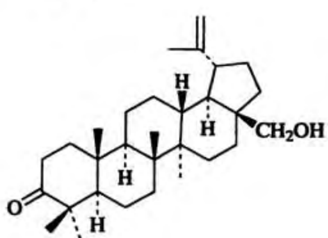
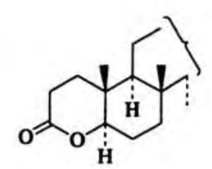
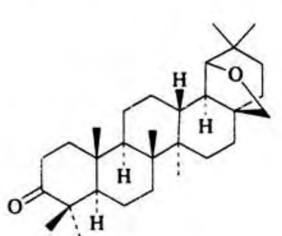
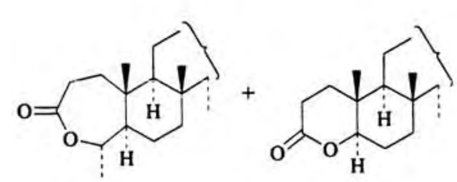
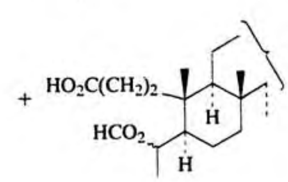
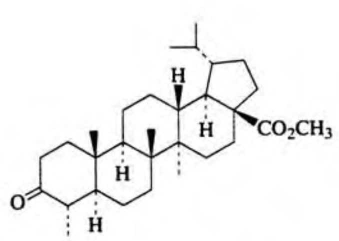
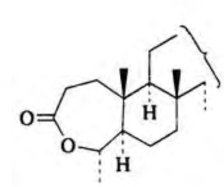
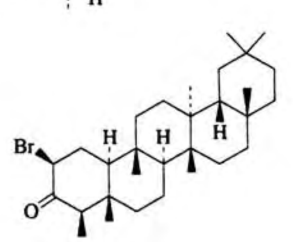
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, NaOH, CH_3OH	 (7)	1045
	H_2O_2, SeO_2	 (—)	1046
	40% PAA, BF_3 etherate, CH_2Cl_2, 16 h, 6°	 (50)	284
	40% PAA, AcOH, 10% H_2SO_4, CH_2Cl_2	 +  (—)	671
	MCPBA, $CHCl_3$, 24 h, 25°	 (88)	622
	PAA, $CHCl_3$, 12 h, reflux	(0)	266

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

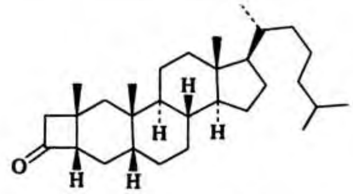
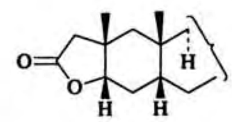
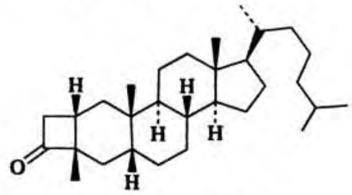
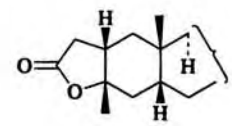
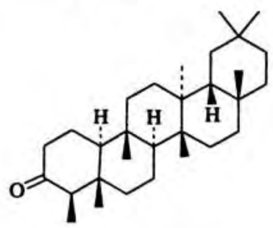
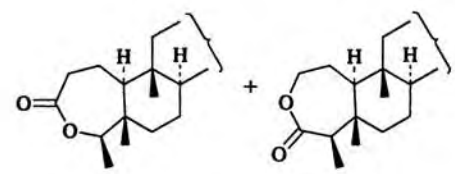
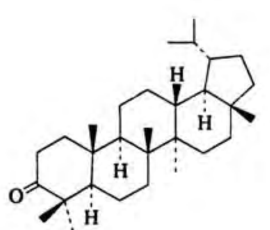
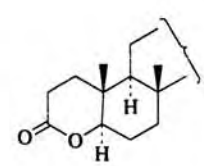
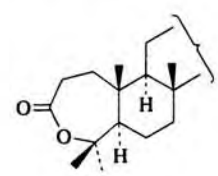
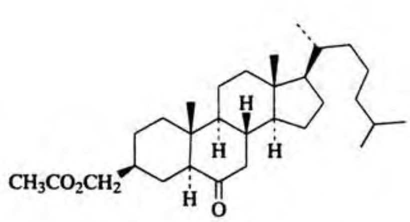
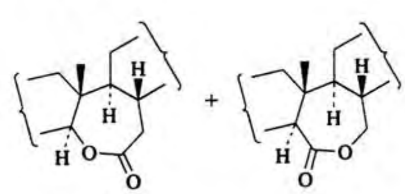
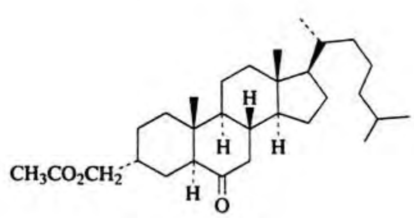
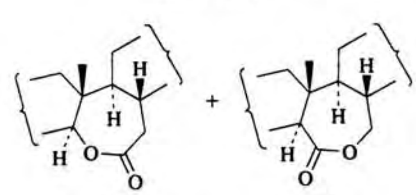
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, NaOH, CH_3OH–THF, 2 h, 25°		(67)	1047
	30% H_2O_2, NaOH, CH_3OH–THF, 12 h, heat		(70)	1047
	MCPBA, TsOH, $CHCl_3$, 4 d, 10°	 I (3) + II (0.4)	(60)*	1048, 1049, 1050
	PNPBA, TsOH, CH_3OH–$CHCl_3$, 30 min, heat	I	(39)	1051
	40% PAA, BF_3 etherate, CH_2Cl_2, 16 h, 6°		(39)	284
	MCPBA, $CHCl_3$, 20 h, 25°		(67)	1052
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II; I:II = 45:55	(100)	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II; I:II = 50:50	(100)	273

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

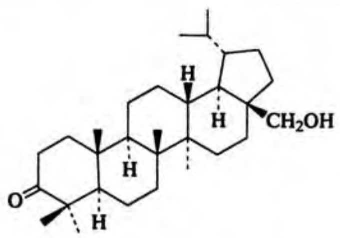
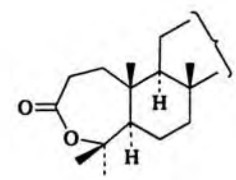
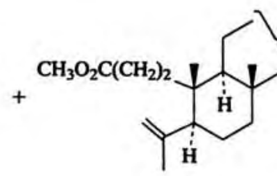
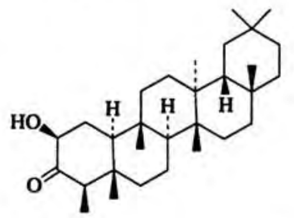
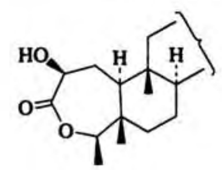
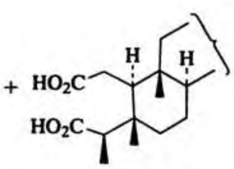
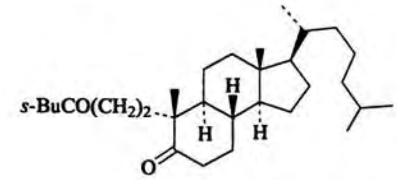
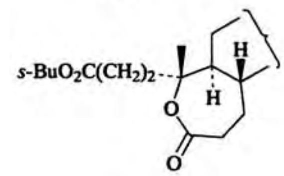
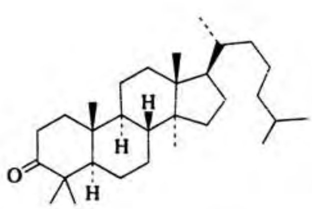
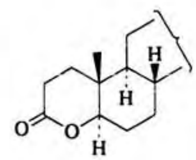
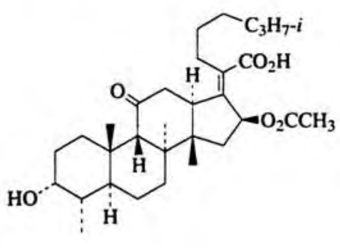
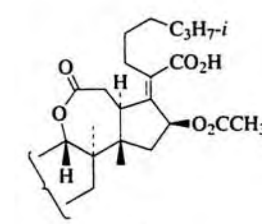
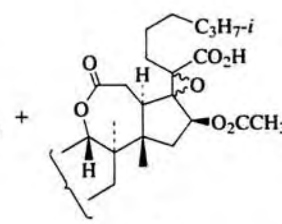
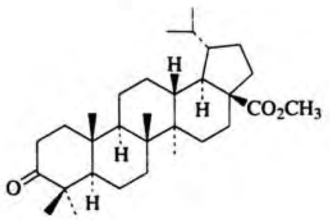
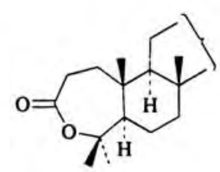
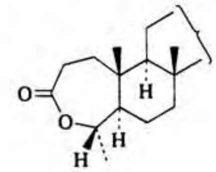
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 6 h, heat	 (8) +  (5) +(50)*	1050
	PAA, $CHCl_3$, 12 h, reflux	 (20) +  (70)	266
	MCPBA	 (—)	1053
	MCPBA, H_2SO_4, AcOH–$CHCl_3$, 5 d, 25°	 (29)	251
C_{31}			
	85% MCPBA, TsOH, CH_2Cl_2, 2 h, 25°	 (32) +  (34)	1054
	MCPBA, CH_2Cl_2, 3.5 h, 25°	 (81)	622
	MCPBA, H_2SO_4–AcOH, CH_2Cl_2, 2 d, 25°	 (92)	622

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

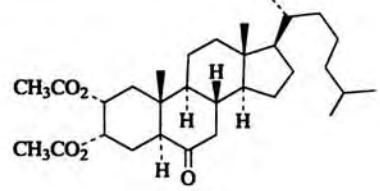
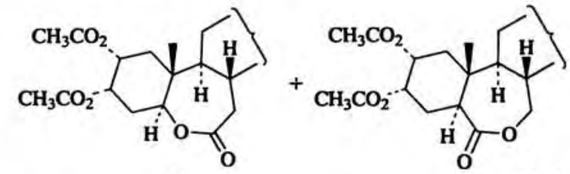
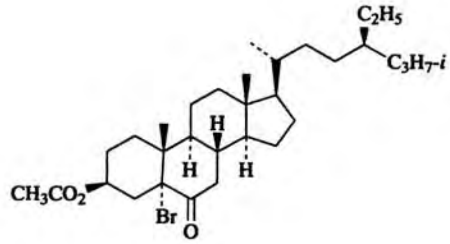
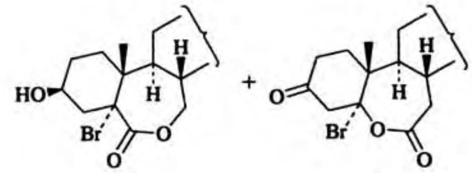
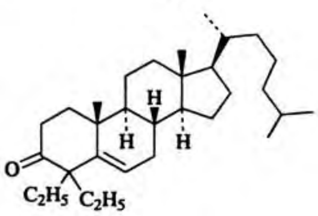
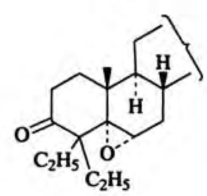
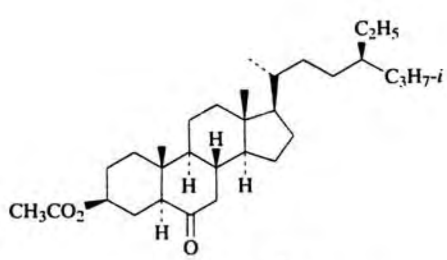
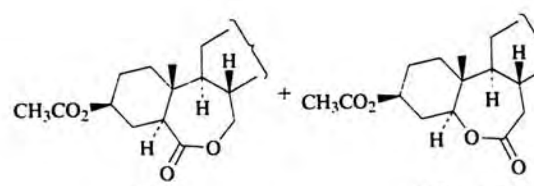
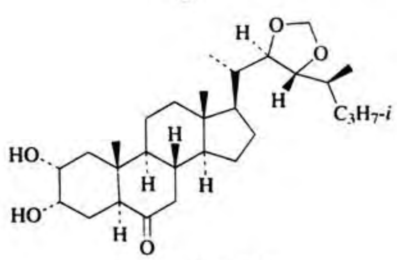
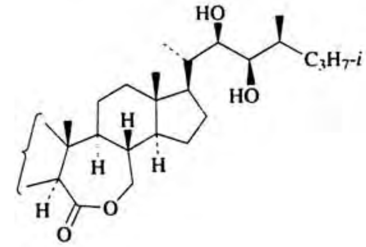
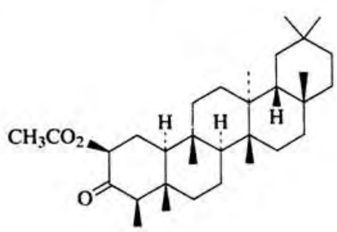
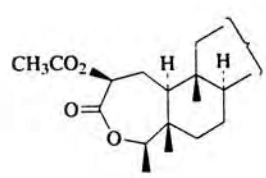
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 14:86	273, 1023
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	I:II = 15:85 (—)	314
	TFPAA, H_2SO_4 (1%)–AcOH (10%), CH_2Cl_2, 25°	I = minor II = major (—)	314
	PBA (2 eq), TsOH, $CHCl_3$, 40 h, 25°	 (16) + (47)	288
	PBA (2 eq), TsOH, $CHCl_3$, 7 d, 25°	 (20)	512
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 (19) + (18) + (25)*	306
 22*R*, 23*R*, 24*S*	TFPAA (30%), CH_2Cl_2, 1 h, 22°	 (74)	1036
C_{32}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 25°	 (—)	266

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

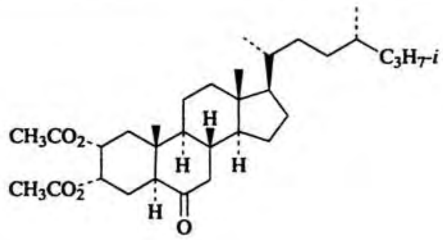
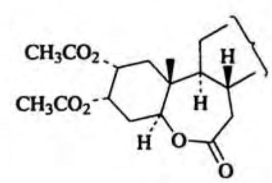
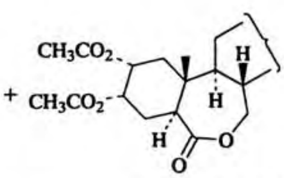
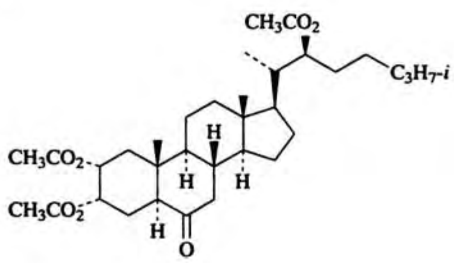
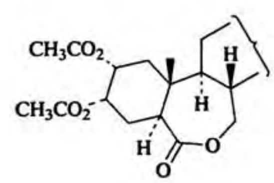
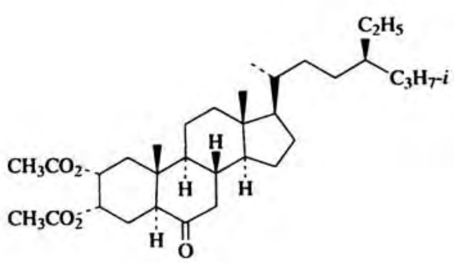
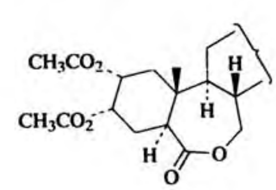
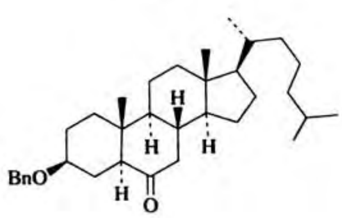
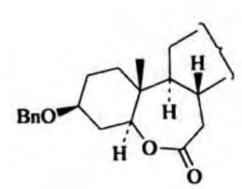
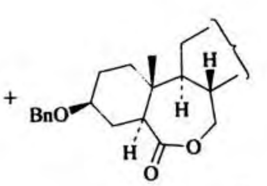
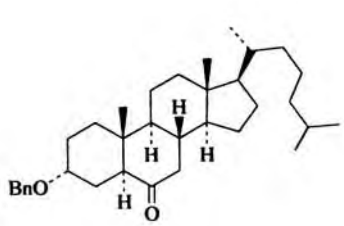
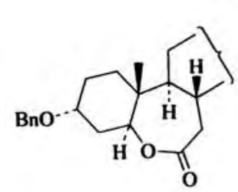
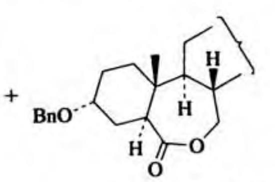
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	 I +  II (—) I:II = 15:85	314
	TFPAA, H_2SO_4 (1%)-AcOH (10%), CH_2Cl_2, 25°	I = major II = minor (—)	314
C_{33}			
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, heat	 (53)	1023
	TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, 25°	 (77)	1055
C_{34}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 33:67	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I +  II (100) I:II = 38:62	273

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

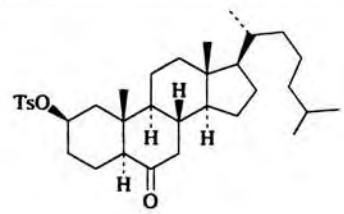
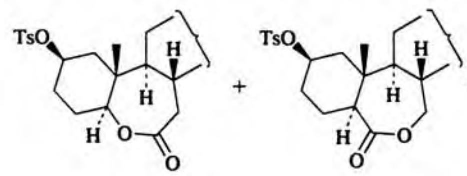
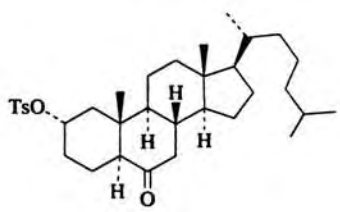
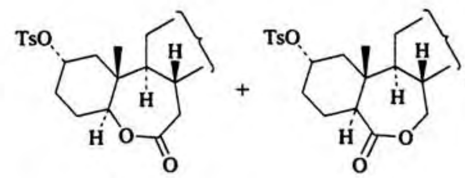
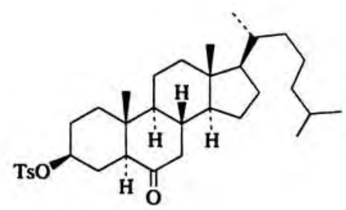
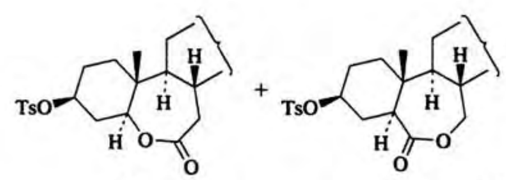
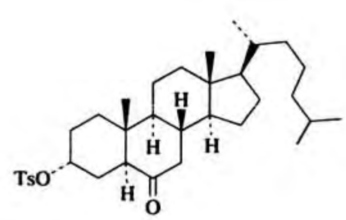
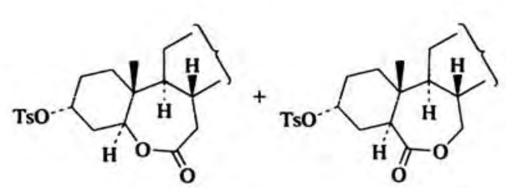
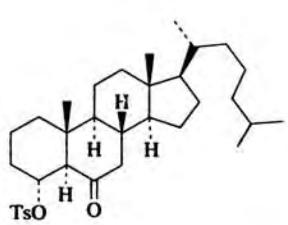
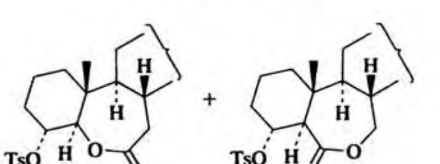
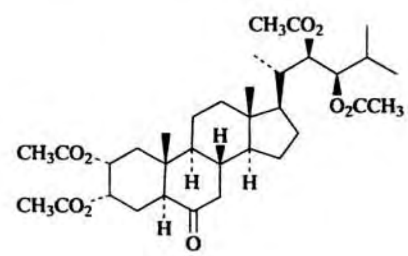
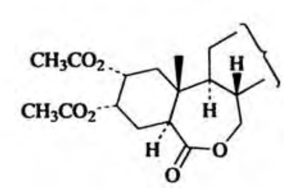
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 27:73	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 20:80	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 25:75	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 28:72	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 20°	 I + II (100) I:II = 14:86	273
	TFPAA, Na_2HPO_4, CH_2Cl_2, 2.5 h, 0°	 (82)	1056, 1057

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

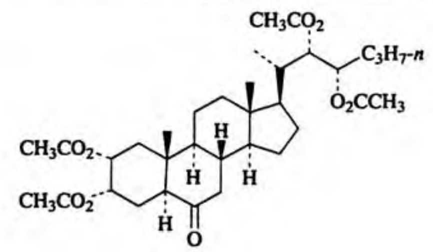
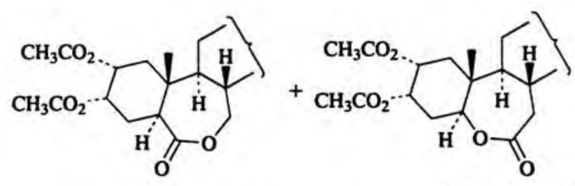
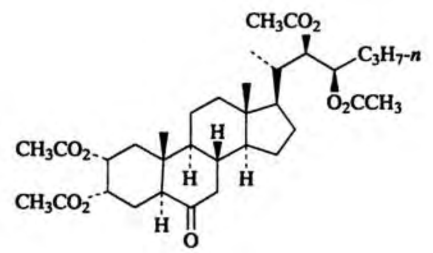
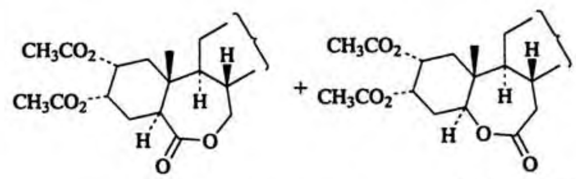
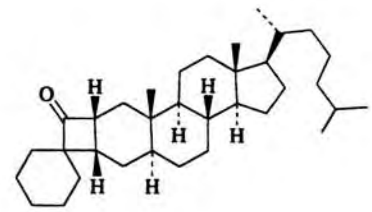
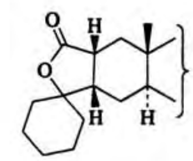
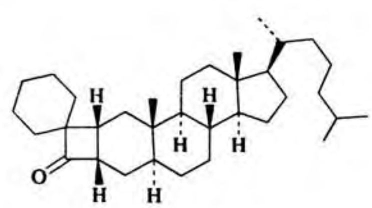
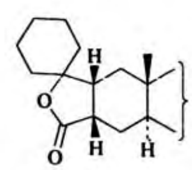
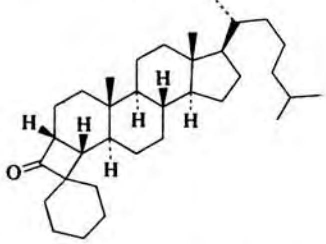
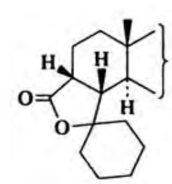
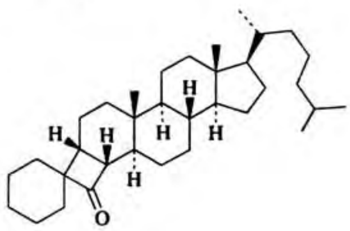
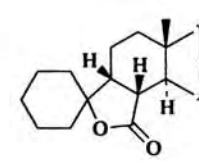
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	 I II (—) I:II = 85:15	314
	TFPAA, H_2SO_4 (1%)–AcOH (10%), CH_2Cl_2, 25°	I minor II major (—)	314
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	 I II (—) I:II = 85:15	314
	TFPAA, H_2SO_4 (1%)–AcOH (10%), CH_2Cl_2, 25°	I = minor II = major (—)	314
	30% H_2O_2, NaOH, THF–CH_3OH, 4 h, 25°	 (96)	246
	30% H_2O_2, NaOH, THF–CH_3OH, 4 h, 25°	 (85)	246
	30% H_2O_2, NaOH, THF–CH_3OH, 4 h, 25°	 (87)	246
	30% H_2O_2, NaOH, THF–CH_3OH, 4 h, 25°	 (85)	246

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TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

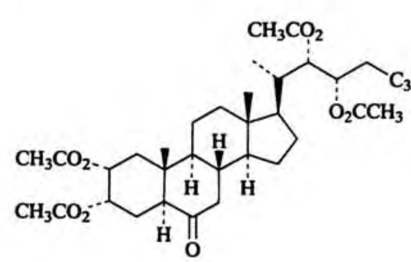
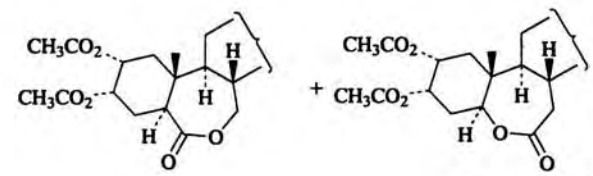
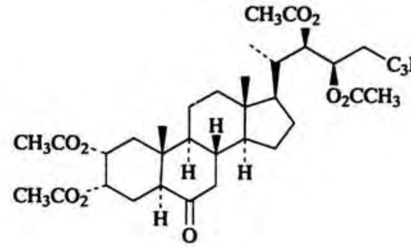
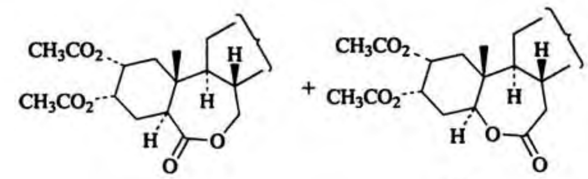
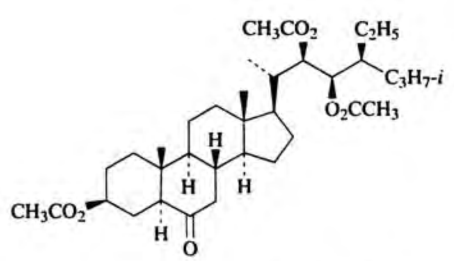
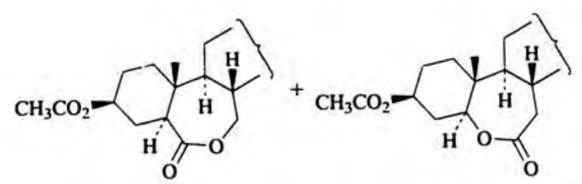
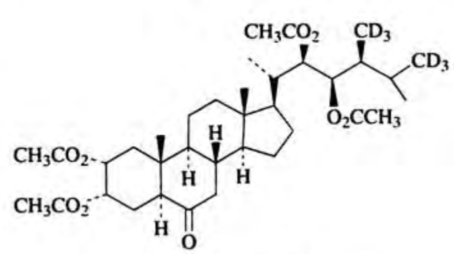
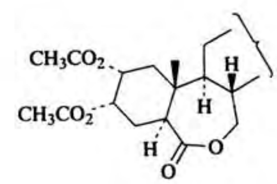
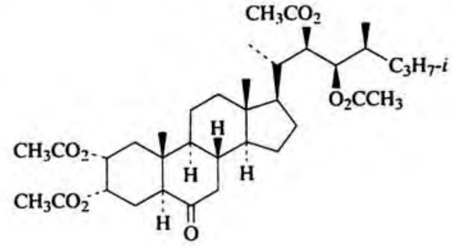
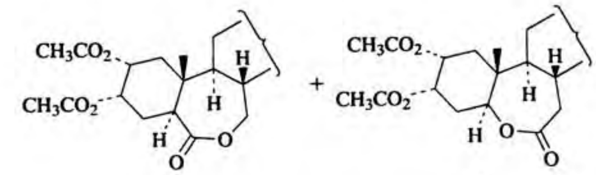
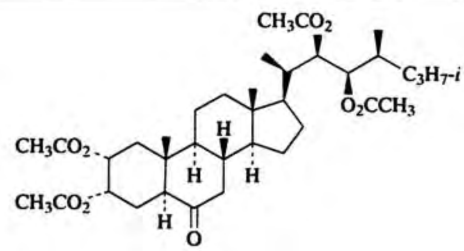
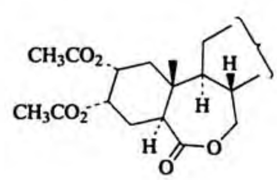
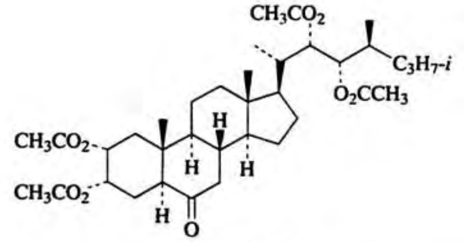
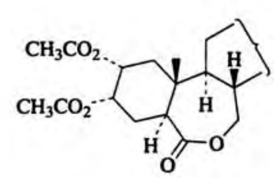
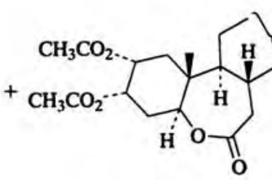
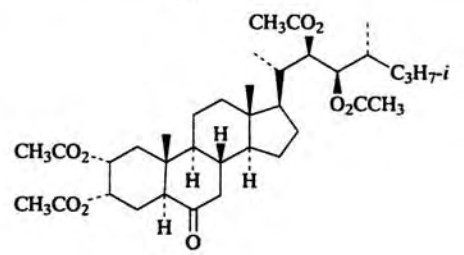
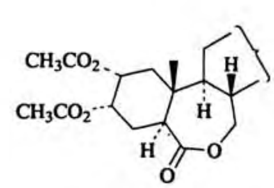
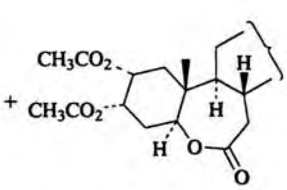
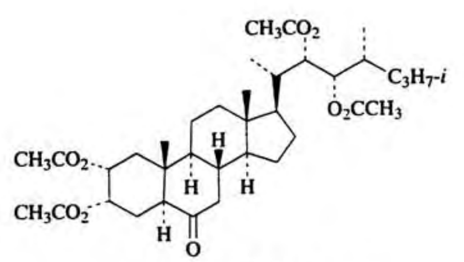
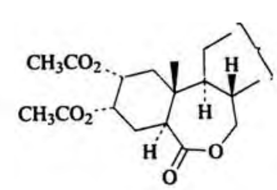
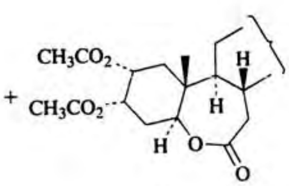
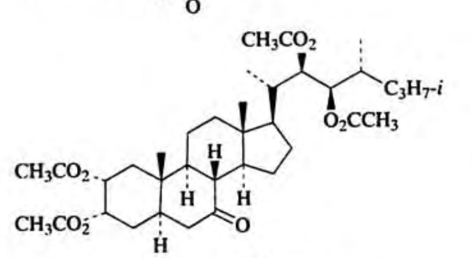
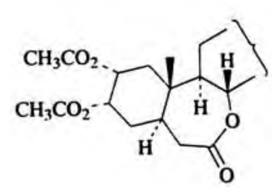
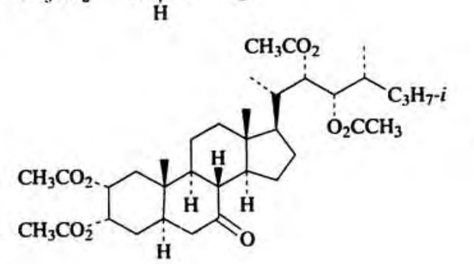
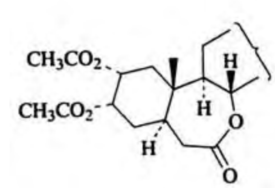
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{35}			
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, 0° 2. 1.5 h, heat	 I (32) + II (3) + (47)*	1058
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	I:II = 85:15 (—)	314
	TFPAA, H_2SO_4 (1%)–AcOH (10%), CH_2Cl_2, 25°	I = minor II = major (—)	314
	TFPAA, CH_2Cl_2, fast, 25°, or MCPBA, $CHCl_3$, 14 d	 I + II I:II = 85:15 (—)	312, 314
	TFPAA, H_2SO_4 (1%)–AcOH (10%), CH_2Cl_2, 25°	I = minor II = major (—)	312, 314
	TFPAA, Na_2HPO_4, CH_2Cl_2, 0°	I:II = 100:0 (>56)	1059
	TFPAA, Na_2HPO_4, CH_2Cl_2, 3 h, 0°	 (56) + (36)	1060
C_{36}			
	TFPAA (30%), Na_2HPO_4, CH_2Cl_2, 1 h, 25°	 (83)	1061
	TFPAA, Na_2HPO_4, CH_2Cl_2, 3 h, 0°	 I + II I:II = 91:9 (80)	312, 313
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 1.5 h, reflux	I:II = 100:0 (83)	1062, 1063, 1064

TABLE III. REACTIONS OF FUSED-RING KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (30%), CH_2Cl_2, 1 h, 0°	 (84)	1065
	TFPAA (50%), CH_2Cl_2, 1.5 h, 25°	 (76) +  (10)	1064
	MCPBA, $CHCl_3$, 14 d, 25°	 major +  minor (—)	1066
	MCPBA, $CHCl_3$, 14 d, 25°	 major +  minor (—)	1066
	TFPAA (30%), CH_2Cl_2, 1 h, 25°	 (96)	736
	TFPAA (30%), CH_2Cl_2, 1 h, 25°	 (78)	736

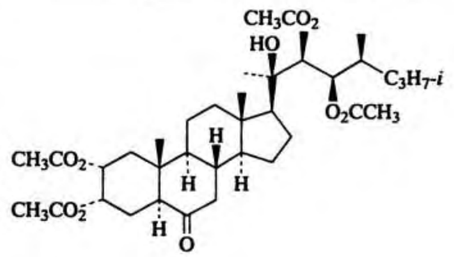
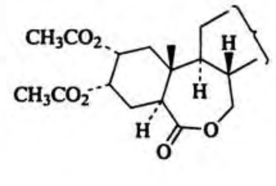
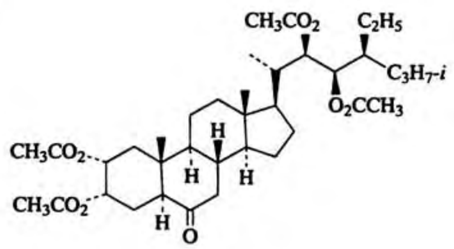
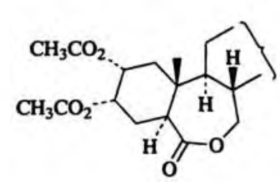
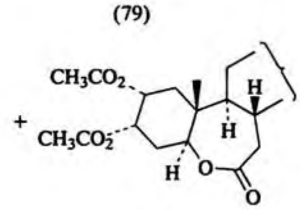
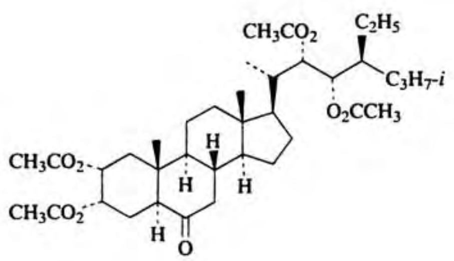
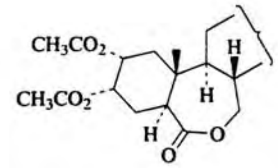
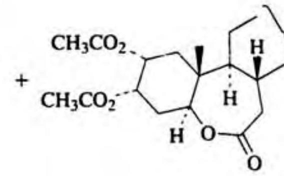
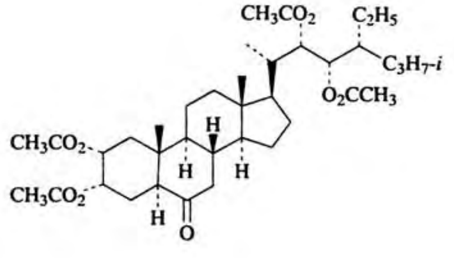
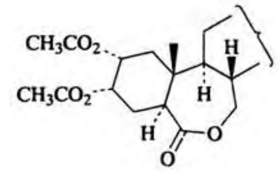
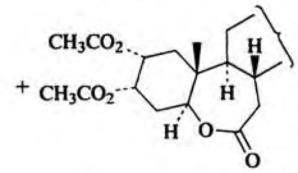
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 3 h, 0°		(77)	1065
C_{37}				
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 30 min, 25° 2. 1 h, heat	 (79) +  (20)		1055, 1067, 1068
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	 I (66) +  II (7)		1058
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.5 h, heat	I	(99)	1062
	MCPBA, $CHCl_3$, 14 d, 25°	 major +  minor	(—)	1066

TABLE III. Reactions of Fused-Ring Ketones (*Continued*)

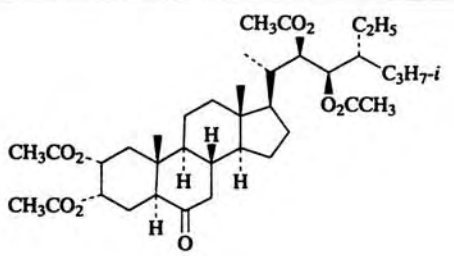
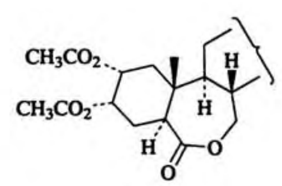
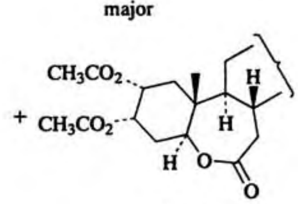
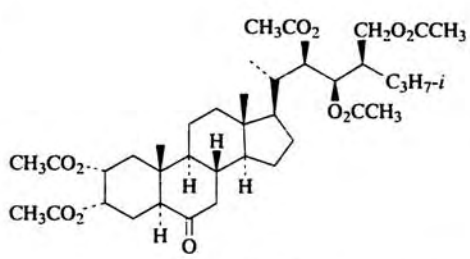
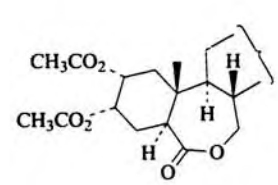
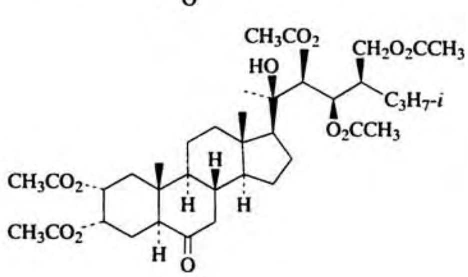
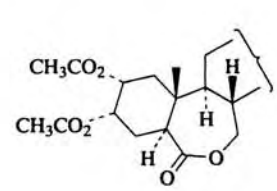
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $CHCl_3$, 14 d, 25°	 major +  minor	(—)	1066
C_{38}				
	TFPAA (30%), CH_2Cl_2, 1 h, 0°		(86)	1065
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 3 h, 0°		(79)	1065

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES

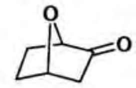
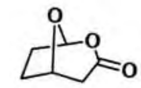
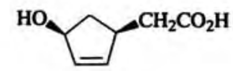
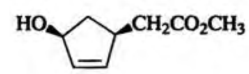
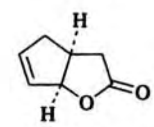
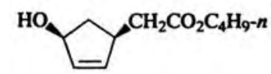
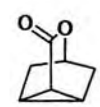
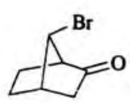
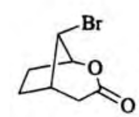
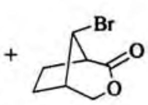
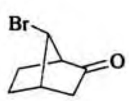
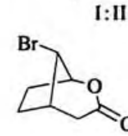
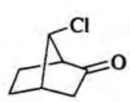
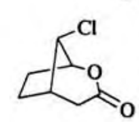
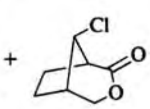
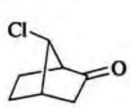
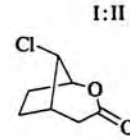
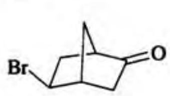
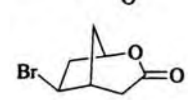
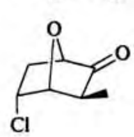
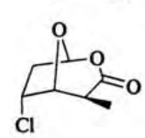
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 h, 25°	 (74)	384
C_7			
	30% H_2O_2, NaOH, ether, 40 min, 10–25°	 (70)	412
	1. 30% H_2O_2, NaOH, ether 2. CH_2N_2, ether	 (41)	408
	40% PAA, NaOAc, $CHCl_3$, 1 h, <0°	 (—)	376
	1. H_2O_2, NaOH, ether, H_2O 2. C_4H_9I, HMPA	 (>70)	389
	PAA	 (56)	1068
	40% PAA, AcOH, NaOAc, 15 d, 25°	 I +  II (73) I:II = 29:71	361, 369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 (71)	369
	40% PAA, AcOH, NaOAc, 14 d, 25°	 I +  II (77) I:II = 47:53	361, 369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 (76)	369
	MCPBA	 (92)	1069
	MCPBA, $NaHCO_3$, $CHCl_3$, 8 h	 (86)	382

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

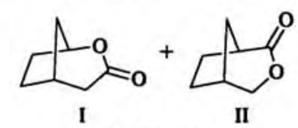
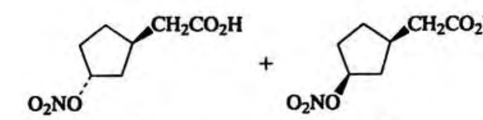
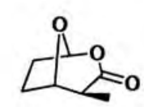
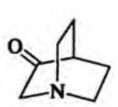
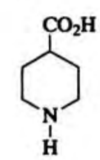
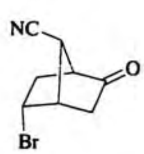
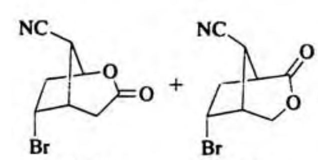
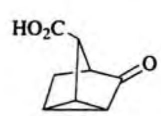
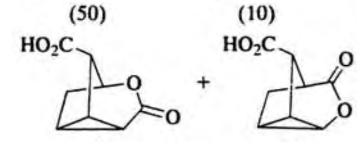
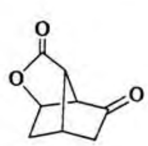
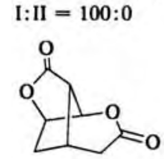
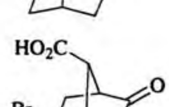
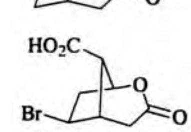
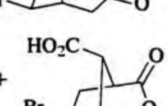
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5 h, 25°	 I II I:II = 92:8	(86)	321, 335, 362
	40% PAA, H_2SO_4, AcOH, 5 d, 27°	I:II = 75:25	(97)	362, 371
	Na_2CO_4, CF_3CO_2H, 0°, 1.5 h	I:II = 86:14	(90)	763a
	TFPAA (85%), Na_2HPO_4, CH_2Cl_2, 10 h	I	(100)	322, 323, 371, 1070
	CAN, CH_3CN–H_2O, 3 h, 60°	 I II I:II = 60:40	(45)	686
	MCPBA, $NaHCO_3$, $CHCl_3$, 112 h, 12°		(94)	383
	30% H_2O_2, C_2H_5OH, 1–14 d		(72)	73
C_8				
	MCPBA, $NaHCO_3$, CH_2Cl_2, 9 h, 25°	 (50) (10)		349
	40% PAA, AcOH, 12 h	 I II I:II = 88:12	(—)	340
	"	I:II = 100:0	(51)	343
	MCPBA, $NaHCO_3$		(75)	1071
	PAA, NaOAc, AcOH, 12 h, 25°	 I	(71)	343
	PAA/AcOH	I +  II I:II = 78:22	(91)	340

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

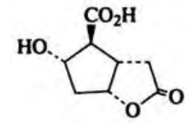
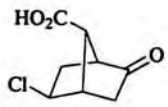
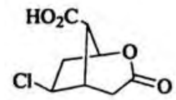
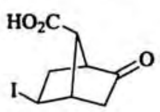
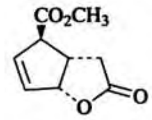
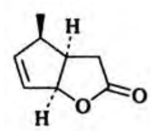
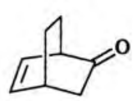
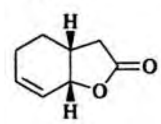
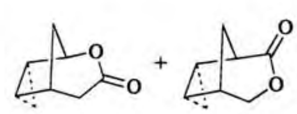
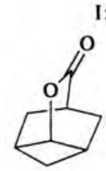
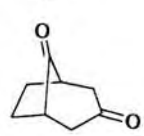
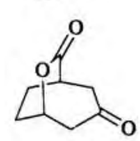
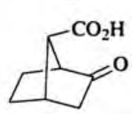
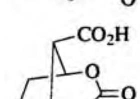
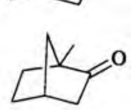
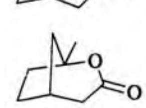
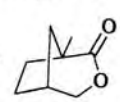
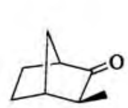
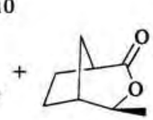
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. PAA, AcOH, H_2SO_4 2. NaOH		(—)	340
	PAA, NaOAc, AcOH, 12 h, 25°		(74)	343, 1071
	1. PAA 2. CH_2N_2		(—)	344
	1. H_2O_2, NaOH 2. BF_3 etherate, CH_2Cl_2		(70)	1072
	28% PAA, NaOAc, AcOH, 3 d, 25°		(80)	371
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 d, 25°		(80)	422
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 d, 25°	 I II I:II = 80:20	(83)	422
	TFPAA (90%), Na_2HPO_4, CH_2CL_2, 6 h, 25°		(98)	374
	MCPBA, CH_2Cl_2, 24 h, 25°		(86)	444
	MCPBA (solid state) or PAA		(83)	371a
	40% PAA, H_2SO_4, AcOH, 2 h, 25°	 I	(42)	362
	30% H_2O_2, Nafion, CH_2Cl_2, 12 h, heat	I +  II I:II = 90:10	(94)	323
	PNPBA, CH_2Cl_2	 (35) +  (35)		360

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

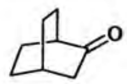
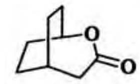
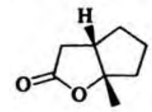
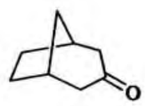
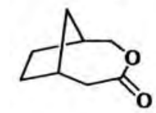
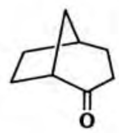
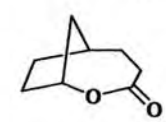
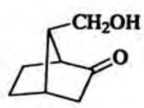
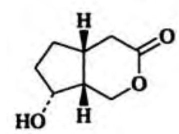
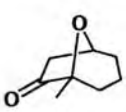
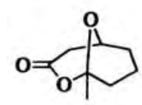
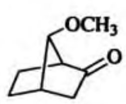
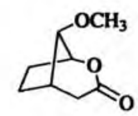
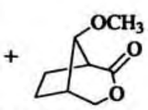
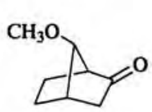
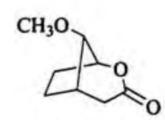
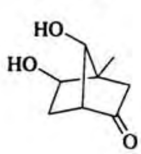
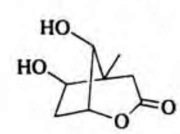
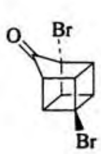
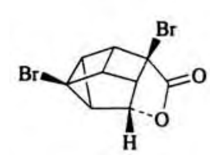
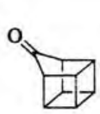
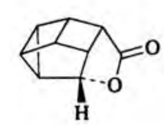
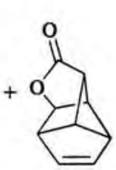
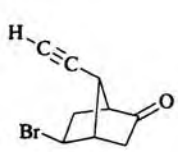
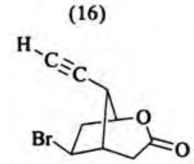
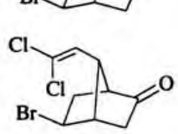
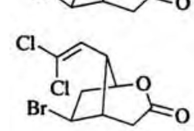
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	28% PAA, NaOAc, AcOH, 5 d, 25°	 (89)	371, 420
	H_2O_2, NaOH	 (100)	656
	MCPBA, CH_2Cl_2, 56 h, 25°	 (81)	444, 445
	MCPBA, CH_3SO_3H, $CHCl_3$, >1.5 h, heat	 (80–90)	431
	MCPBA, $NaHCO_3$, CH_2Cl_2	 (76)	371b
	MCPBA, $NaHCO_3$, CH_2Cl_2	 (quant)	442
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I +  II (69) I:II = 45:55	369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 (79)	369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 h, 23°	 (95)	329
C_9			
	CAN, $CH_3CN–H_2O$, 30 min, 0–5°	 (15)	687
	CAN, $CH_3CN–H_2O$, 30 min, 0–5°	 (16) +  (6)	687
	MCPBA, CH_2Cl_2, 72 h, 25°	 (79)	352
	70% MCPBA, CH_2Cl_2, 24 h, 25°	 (89)	353

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

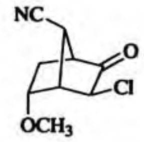
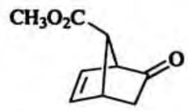
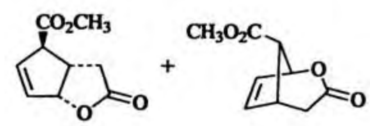
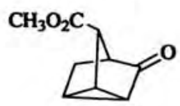
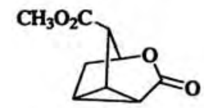
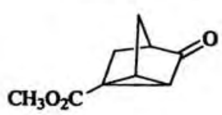
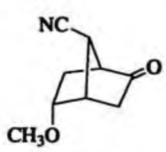
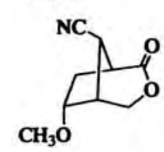
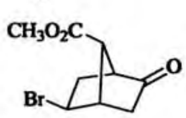
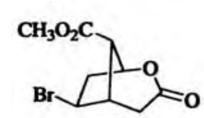
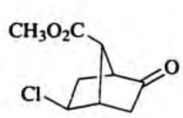
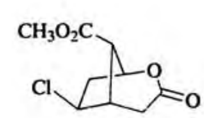
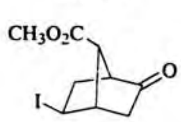
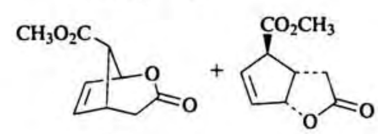
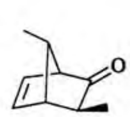
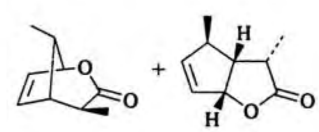
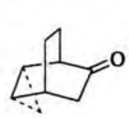
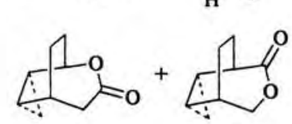
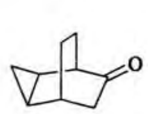
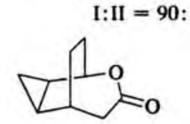
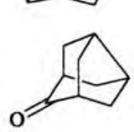
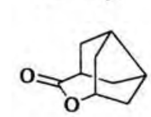
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	—	no reaction		349
	MCPBA		(—)	343, 344
	MCPBA, CH_2Cl_2		(100)	343
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°		(90)	375
	MCPBA, $NaHCO_3$, CH_2Cl_2, 3 h, 25°		(65)	349
	MCPBA, CH_2Cl_2		(70)	343
	MCPBA, CH_2Cl_2, 7 h, 0–20°		(76)	346
	40% PAA, NaOAc, $CH_3CO_2C_2H_5$, 35 h, 25°	 I major, II trace	(81)	343, 344
	1. 40% PAA, NaOAc, $CH_3CO_2C_2H_5$, 35 h, 25° 2. TsOH, benzene	I:II = 0:100	(81)	344
	1. MCPBA, $NaHCO_3$, CH_2Cl_2, 23 h, 5° 2. BF_3 etherate		(84)	416
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5 d, 25°	 I, II; I:II = 90:10	(97)	422
	MCPBA, $NaHCO_3$, CH_2Cl_2, 2 d, 25°		(62)	422
	TFPAA, Na_2HPO_4		(80)	473

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

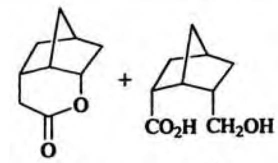
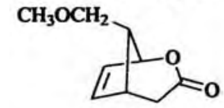
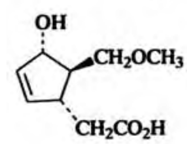
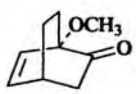
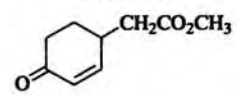
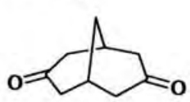
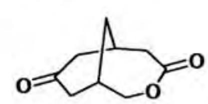
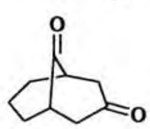
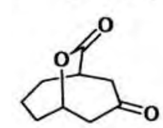
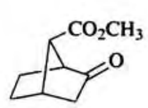
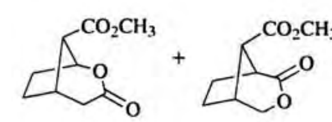
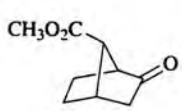
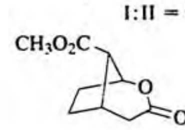
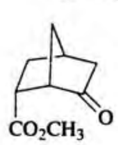
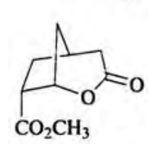
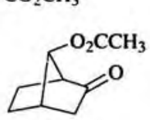
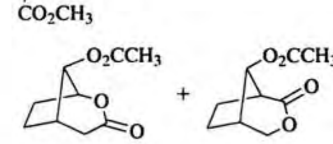
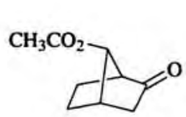
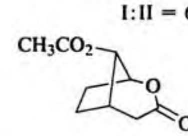
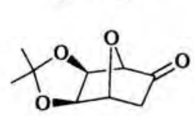
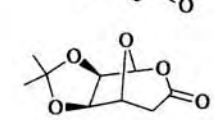
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1.25 h, 0°-heat	 I II I:II = 55:45 (84)	437
	MCPBA, $NaHCO_3$, CH_2Cl_2	 (95)	392
	30% H_2O_2, NaOH, 40 min, 10–25°	 (99)	390
	1. 40% PAA (1 eq), NaOAc, AcOH, 3 h, 50° 2. 40% PAA (1 eq), 72 h, 25° 3. K_2CO_3, $(CH_3)_2SO_4$, acetone, 3 h, reflux	 (85)	423, 753
	MCPBA, CH_2Cl_2, 12 h, 25°	 (79)	466, 469
	MCPBA, 16 h, 25°	 (89)	444
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 95:5 (78)	369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 (78)	359, 369
	PAA, AcOH	 (—)	358
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 60:40 (80)	369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 (80)	369
	MCPBA, CH_2Cl_2, 3 d, 25°	 (87)	387

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

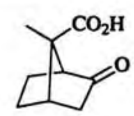
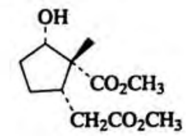
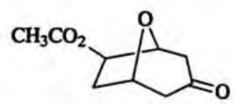
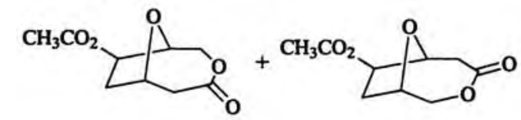
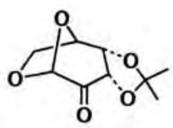
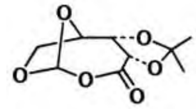
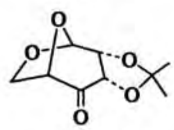
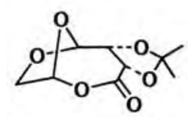
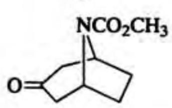
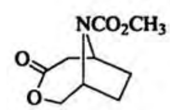
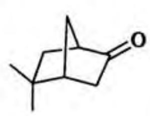
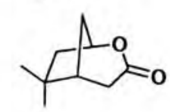
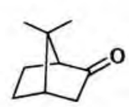
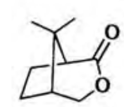
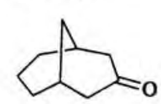
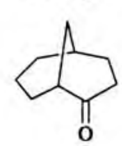
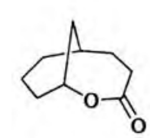
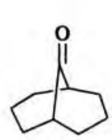
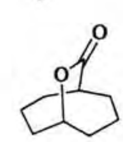
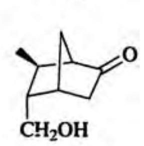
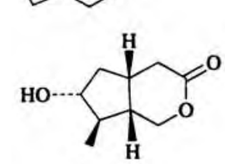
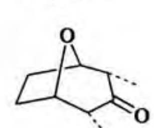
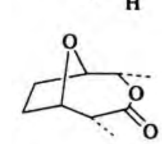
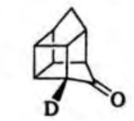
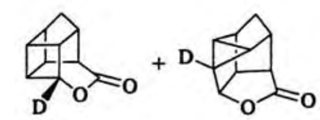
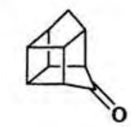
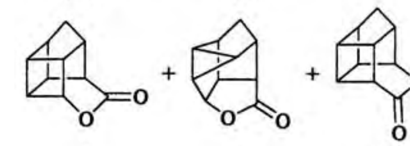
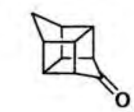
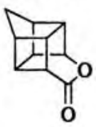
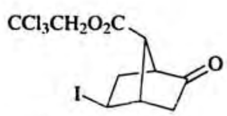
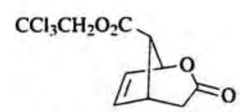
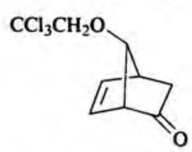
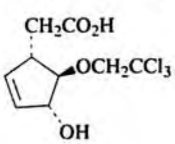
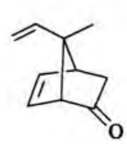
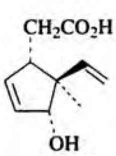
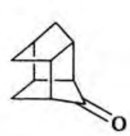
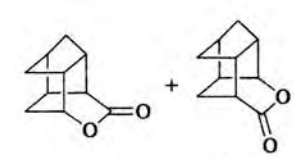
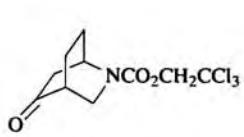
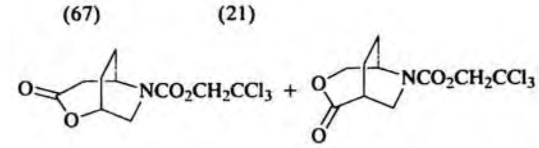
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 80% H_2O_2, 40% NaOH, 7 d, 18° 2. CH_2N_2	 (34)	356
	TFPAA, CH_2Cl_2, 12 h, 15°	 I + II I:II = 46:54 (78)	38, 39
	MCPBA, $CHCl_3$, <2 h, 25°	 (45)	301
	MCPBA, $CHCl_3$, <2 h, 25°	 (74)	301
	MCPBA, $ClCH_2CH_2Cl$, 65°, 24 h, 2,6-$(t\text{-}C_4H_9)_2$-4-$CH_3C_6H_2OH$	 (24) (76)*	1073
	1. MCPBA, Na_2HPO_4, CH_2Cl_2, 6 h, 0° 2. 18 h, 25°	 (84)	354
	K_2SO_5, H_2SO_4, ligroin	 (18)	367
	MCPBA, CH_2Cl_2, heat	(0)	444, 466
	MCPBA, CH_2Cl_2, 3 h, 25°	 (83)	444
	TFPAA (73%), CH_2Cl_2, 6 h, reflux	" (28)	464
	40% PAA, NaOAc, AcOH, 65 h, 25°	 (82)	471
	MCPBA, CH_2Cl_2	 (—)	355
	1. TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 2 h, 25° 2. 15 min, heat	 (94)	447

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	MCPBA, $CHCl_3$, 1 h, 25°	 (57) (16)	377
	MCPBA, $CHCl_3$, 1 h, 25°	 I (50) II (13) III (1)	377, 380
	$Pb(OAc)_4$, AcOH, 3 h, heat	II (55) +(21)*	377
	85% MCPBA, benzene, 15 min, 25°	I + II (56) (12)	377, 378
	MCPBA, dioxane–H_2O, 1 h, 25°	I + II (46) (31)	377, 380
	CAN, CH_3CN–H_2O, 1 h, 60°	II (78)	378
	CAN, CH_3CN–H_2O	II (—)	380
	30% H_2O_2, Nafion-H, CH_2Cl_2, 1 h, reflux	I + III (90) I:III = 50:50	323, 974
	MCBPA, TsOH, benzene, 2 h, 25°	 (86)	378, 974
	40% PAA, NaOAc, $CH_3CO_2C_2H_5$, 12 h, 25°	 (100)	343
	30% H_2O_2, NaOH, 40 min, 10–25°	 (>95)	390, 394
	30% H_2O_2, NaOH, CH_3OH–H_2O, 12 h, 0°	 (85)	393
	MCPBA, $CHCl_3$, 9 h, 25°	 (67) (21)	377
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II (83) I:II = 70:30	424
	PAA, NaOAc, AcOH, 24 h, 25°	I:II = 100:0 (76)	424

624

625

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

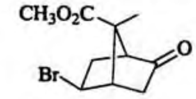
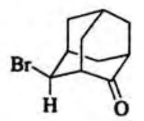
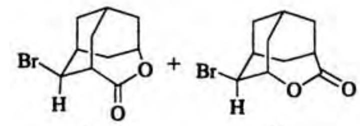
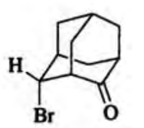
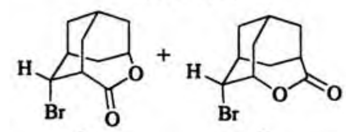
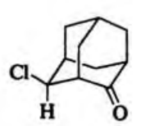
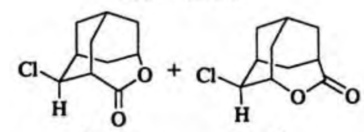
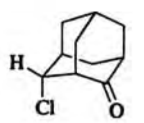
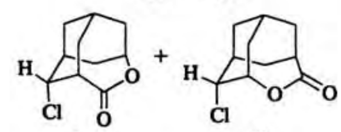
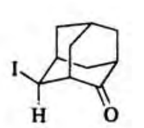
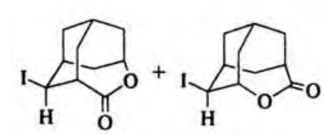
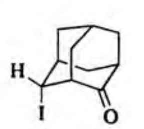
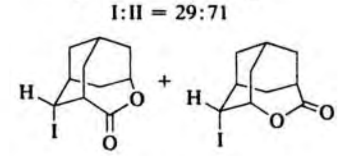
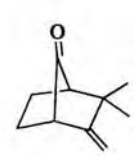
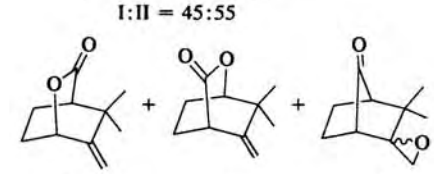
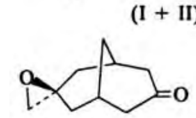
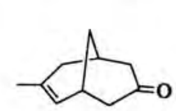
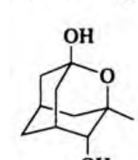
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, NaOH	(0)	396
	MCPBA, CH_2Cl_2, 12 h, 20°	 I II I:II = 95:5 (75)	476
	PAA, AcOH, 12 h, 60°	 I II I:II = 80:20 (50) (45)*	476
	MCPBA, CH_2Cl_2, 12 h, 20°	 I II I:II = 94:6 (81)	476
	PAA, AcOH, 14 h, 60°	 I II I:II = 93:7 (67) (32)*	476
	SeO_2, H_2O_2, *t*-BuOH, 100 h, 20°	 I II I:II = 29:71 (69)	476
	SeO_2, H_2O_2, *t*-BuOH, 100 h, 20°	 I II I:II = 45:55 (36) (56)*	476
	PAA	 I II III (I + II):III = 80:20 (—)	1074
	MPPA, $CHCl_3$, 10–12 h, 25°	 (89)	468
	MPPA, $CHCl_3$, 3 h, 25°	 (82)	467

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

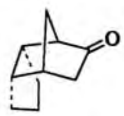
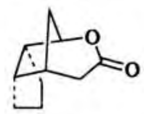
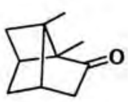
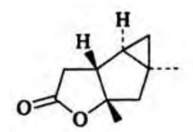
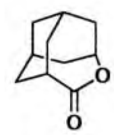
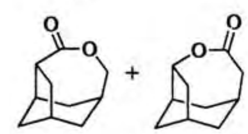
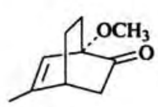
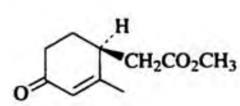
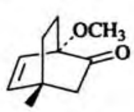
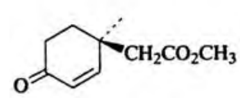
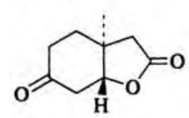
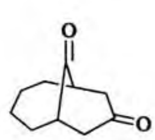
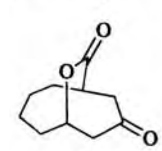
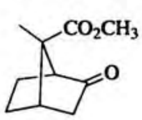
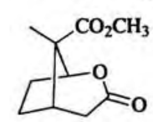
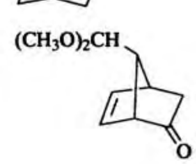
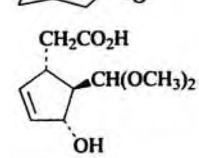
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, 12 h, reflux		(100)	323
	PBA, benzene, 5 d, 25°		(78)	364
	PBA, TsOH, benzene, 4 d, 25°		(60)	364
	MCPBA, CH_2Cl_2, 12 h, reflux		(100)	47, 323, 686, 763a, 974, 1075–1079
	MCPBA, CH_2Cl_2, 3 d, 25°	 I + II; I:II = 35:65	(93)	478
	1. 40% PAA (1 eq), NaOAc, AcOH, 3 h, 50° 2. 40% PAA (1 eq), 96 h, 25° 3. 10% NaOH, $(CH_3)_2SO_4$, 2 h, 25°		(59)	423, 753
	1. 40% PAA (1 eq), NaOAc, AcOH, 3 h, 50° 2. 40% PAA (1 eq), 48 h, 25° 3. K_2CO_3, $(CH_3)_2SO_4$, acetone, 1 h, reflux		(80)	423, 753
	1. 40% PAA (1 eq), NaOAc, AcOH, 4 h, 50° 2. 40% PAA (1 eq), 48 h, 25°		(56)	423, 753
	MCPBA, CH_2Cl_2, 24 h, 25°		(85)	444
	PAA, AcOH		(97)	358
	29% H_2O_2, NaOH, toluene, 4 h, 0°		(>54)	410

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

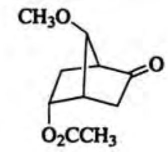
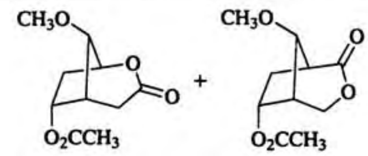
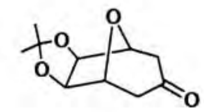
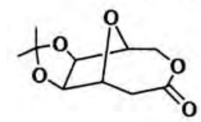
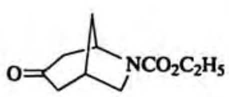
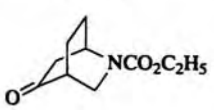
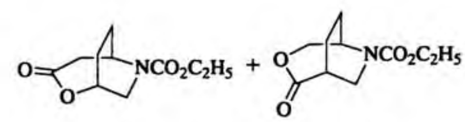
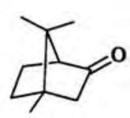
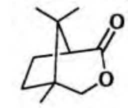
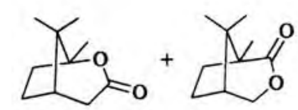
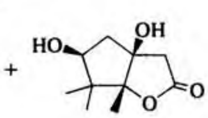
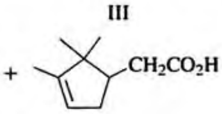
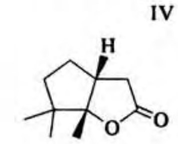
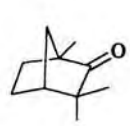
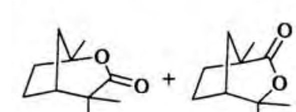
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, HCO_2H, 12 h	 I II I:II = 70:30	(81)	349
	TFPAA (90%), 1 h, 25°		(92)	448
	PNPBA, $NaHCO_3$, CH_2Cl_2, 7 d, 25°		(0)	1073
	MCPBA, $NaHCO_3$, CH_2Cl_2, 42 h, 25°	 I II I:II = 70:30	(80)	424
	PAA, NaOAc, AcOH, 18 h, 25°	I:II = 100:0	(80)	424
	40% PAA, NaOAc, AcOH, 5 d, 25°		(94)	362
	40% PAA, NaOAc, AcOH, 5 d, 25°	 I II I:II = 75:25	(82)	362, 366
	MCPBA, TsOH, CH_2Cl_2, 7 d, 25°	I:II = 63:37	(78)	363
	H_2SO_5	II	(—)	668
		+  III	(10–15)	
		+  IV		
	1. 40% PAA, NaOAc, AcOH, 5 d, 25° 2. H_2SO_4	 V + II II:V = 25:75	(68)	666
	40% PAA, H_2SO_4, AcOH–H_2SO_4, 5 d, 27°	I	(21)	366
	PAA, NaOAc, AcOH, 14 d, 25°	 I II I:II = 40:60	(35)	362

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

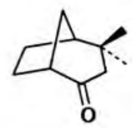
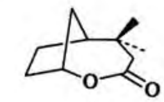
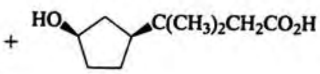
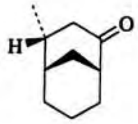
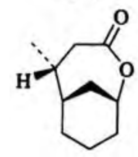
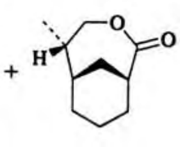
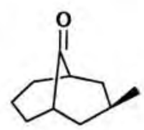
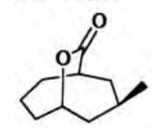
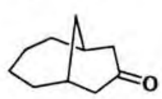
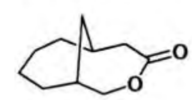
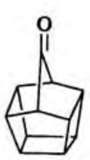
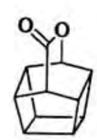
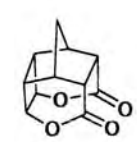
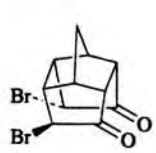
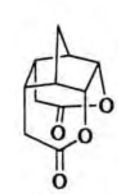
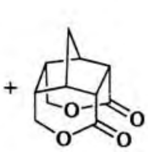
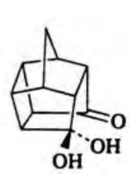
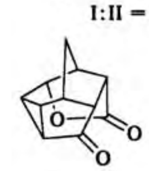
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, AcOH, 7 d, 25°	 (48) +  (27)	428, 429
	MCPBA, CH_2Cl_2, 3 h, 25°	 I +  II I:II = 85:15 (95)	465
	40% PAA, NaOAc, AcOH, 24 h, 25°	I:II = 92:8 (50)	465
	MPPA, ether, 100 h, 25°	 (80)	472
	MCPBA, CH_2Cl_2, 240 h, 25°	 (78)	444
C_{11}			
	70% MCPBA, CH_2Cl_2, 12 h, 25°	 (90)	381
	MCPBA, TsOH, CH_2Cl_2, 48 h, reflux	 (81)	378, 438, 439, 974
	CAN, CH_3CN–H_2O, 1 h, 30°	 (—)	378, 689
	MCPBA or TFPAA, CH_2Cl_2, reflux	(0)	438
	TFPAA (90%), CH_2Cl_2, 15 h, 25°	 I +  II I:II = 5:95 (75)	438
	$Pb(OAc)_4$, C_6H_6–C_5H_5N, 6 h	 (80)	690

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

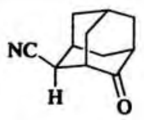
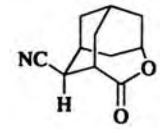
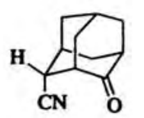
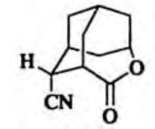
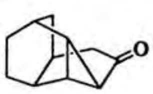
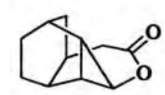
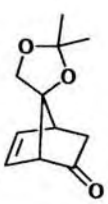
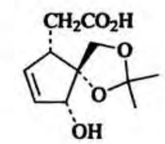
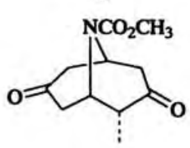
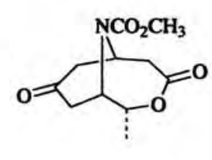
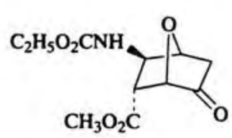
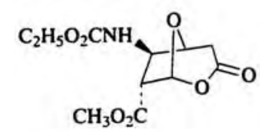
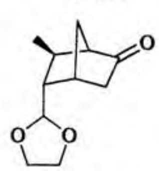
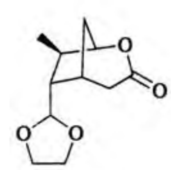
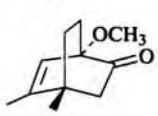
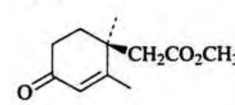
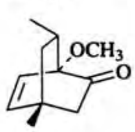
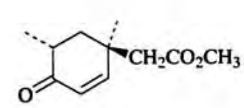
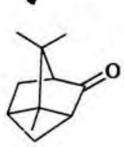
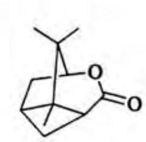
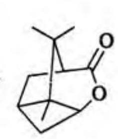
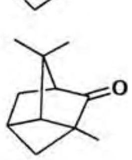
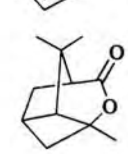
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, AcOH, 12 h, 50°		(63)	476
	PAA, AcOH, 12 h, 70°		(50)	476
	MCPBA, CH_2Cl_2, 48 h		(88)	444
	50% H_2O_2, NaOH, CH_3OH–H_2O, 17 h, 5°		(97)	406
	MCPBA, 4,4′-thiobis-(6-*t*-C_4H_9-*m*-cresol), CH_2Cl_2, reflux		(93)	470
	MCPBA, $CHCl_3$, 1 h, 20°		(—)	385
	MCPBA, CH_2Cl_2		(75)	355
	1. 40% PAA (1 eq), NaOAc, AcOH, 3 h, 50° 2. 40% PAA (1 eq), 72 h, 25° 3. 10% NaOH, $(CH_3)_2SO_4$, 2 h, 25°		(60)	423, 753
	1. 40% PAA (1 eq), NaOAc, AcOH, 3.5 h, 50° 2. 40% PAA (1 eq), 72 h, 25° 3. 10% NaOH, $(CH_3)_2SO_4$, 2 h, reflux		(60)	753
	90% H_2O_2, BF_3 etherate, ether, 70 h, 25°	 + 	(55) + (40)*	372
	90% H_2O_2, BF_3 etherate, ether, 70 h, 25°		(76) (20)*	372

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

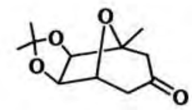
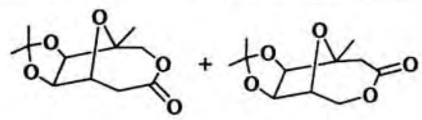
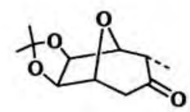
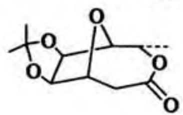
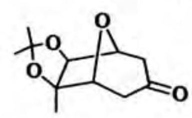
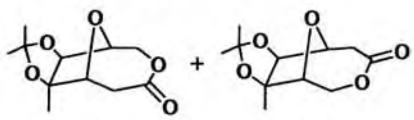
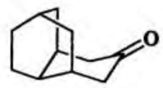
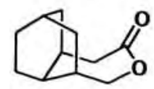
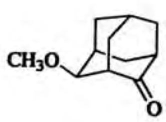
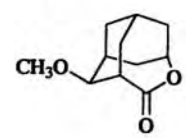
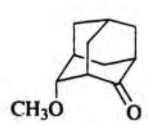
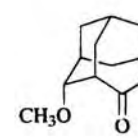
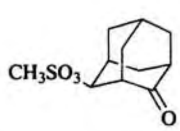
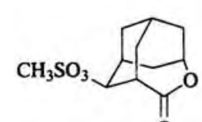
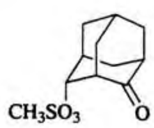
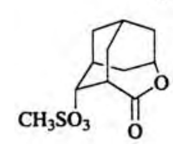
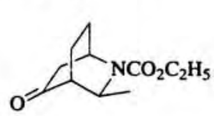
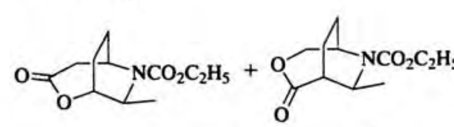
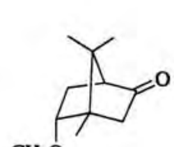
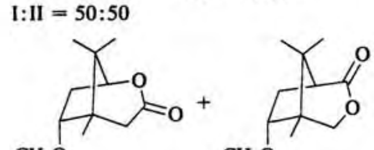
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 10 h, 20–25°	 I II I:II = 53:47	(90)	38, 39
	TFPAA, Na_2HPO_4, CH_2Cl_2, 16 h, 25°		(85)	38
	TFPAA, CH_2Cl_2, 36 h, 25°	 I II I:II = 67:33	(52) (38)*	40
	MCPBA, CH_2Cl_2, 70 h		(86)	444
	PAA, AcOH, 14 h, 20°		(75)	476
	PAA, AcOH, 24 h, 40°		(31)	476
	SeO_2, H_2O_2, *t*-BuOH, 30 h, 20°		(82)	476
	PAA, AcOH, 30 h, 40°		(81)	476
	40% PAA, NaOAc, AcOH, 72 h, 25°	 I II I:II = 62:38	(60)	424
	MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h, 25°	I:II = 50:50	(73)	424
	9% PAA, NaOAc, AcOH, 10 d, 25°	 I minor II major	(67)	368

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

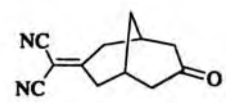
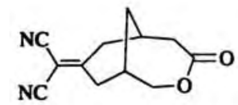
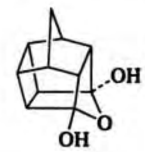
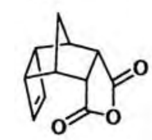
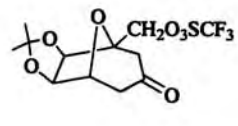
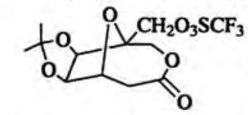
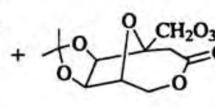
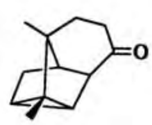
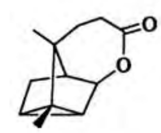
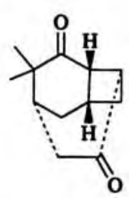
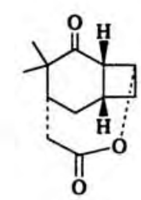
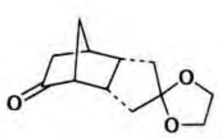
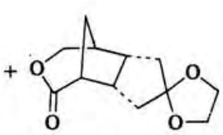
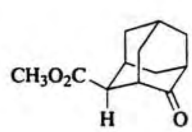
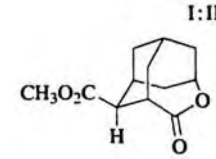
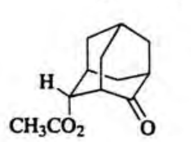
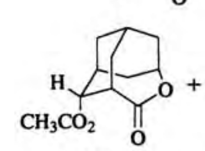
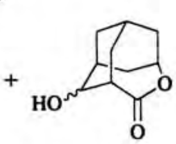
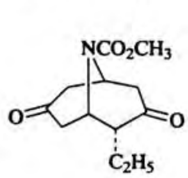
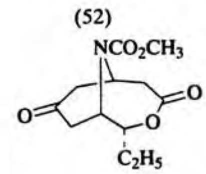
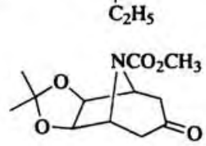
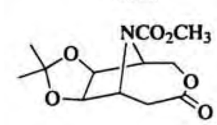
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
	MCPBA, CH_2Cl_2, 9 d, reflux	 (15)	466, 469
	$Pb(OAc)_4$, C_6H_6–C_5H_5N, 8 h	 (25) +  (20)	690
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I +  II (89) I:II = 14:86	38, 39
	—	 (—)	430
	MCPBA, $NaHCO_3$, CH_2Cl_2, 3 d, 25°	 (60)	479
	MCPBA, $NaHCO_3$, CCl_4, 45 h, 25°	 I +  II (100) I:II = 75:25	334, 1080
	PAA, AcOH, 30 h, 20°	 (76)	476
	PAA, AcOH, 16 h, 80°	 (52) +  (9)	476
	MCPBA, 4,4'-thiobis(6-*t*-C_4H_9-*m*-cresol), CH_2Cl_2, reflux	 (94)	470
	MCPBA, 2,4,6-(*t*-C_4H_9)$_3C_6H_2OH$, $ClCH_2CH_2Cl$, 22 h, 55°	 (60)	446

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

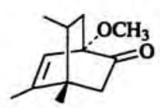
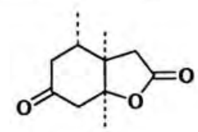
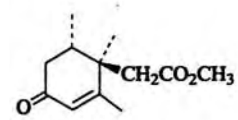
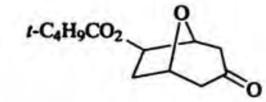
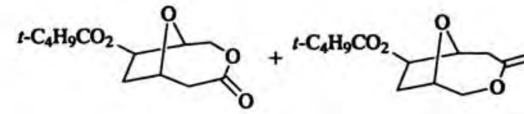
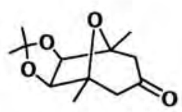
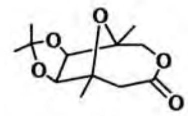
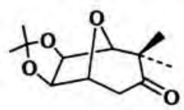
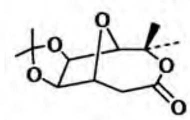
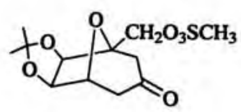
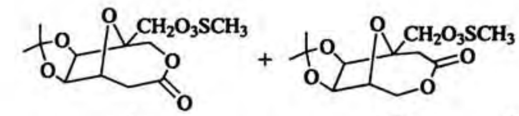
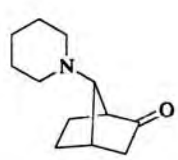
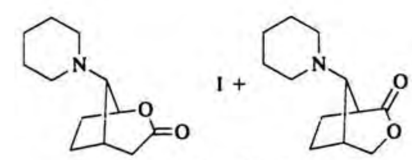
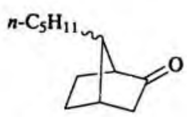
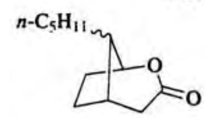
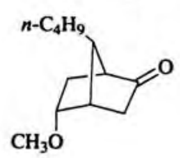
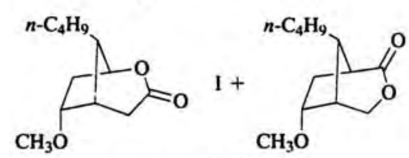
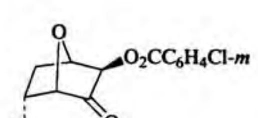
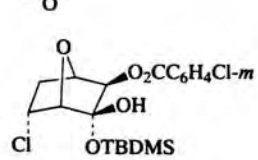
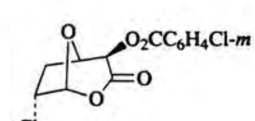
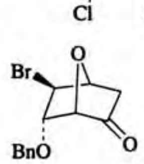
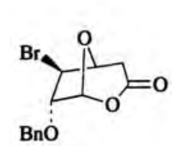
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 40% PAA (1 eq), NaOAc, AcOH, 4 h, 50° 2. 40% PAA (1 eq), 96 h, 25°	 (17)	423
	1. 40% PAA (1 eq), NaOAc, AcOH, 2 h, 50° 2. 40% PAA (1 eq), 48 h, 25° 3. K_2CO_3, $(CH_3)_2SO_4$, acetone, 2 h, reflux	 (52)	423
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 15°	 I + II (89) I:II = 35:65	38, 39
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 13 h, 20°	 (77)	38, 453, 454
	TFPAA, Na_2HPO_4, CH_2Cl_2, 6 h, 25°	 (81)	38, 453
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h, 25°	 I + II (93) I:II = 20:80	39
	1. MCPBA, CH_2Cl_2, 25°, 17–20 h 2. $NaHSO_3$	 I + II (65) I:II = 89:11	371c
	6% PAA, H_2SO_4, AcOH, 12 h, 0°	 (75)	365
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 I + II (73) I:II = 80:20	349
	30% H_2O_2, NaOAc, AcOH, 36 h, 25°	I:II = 100:0 (—)	349
C_{13}			
 via 	MCPBA, $NaHCO_3$, CH_2Cl_2, 66 h, 20°	 (79)	388
	MCPBA, $NaHCO_3$, CH_2Cl_2, 5–20°	 (96)	386

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

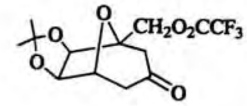
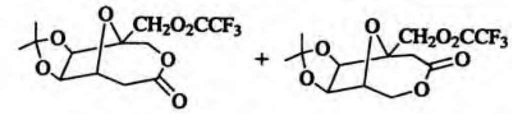
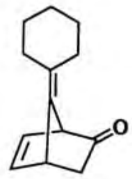
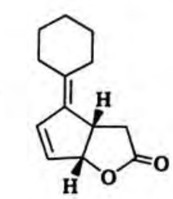
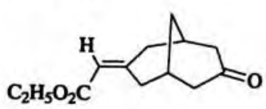
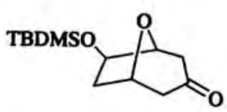
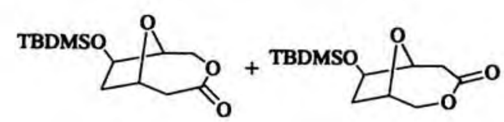
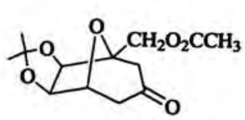
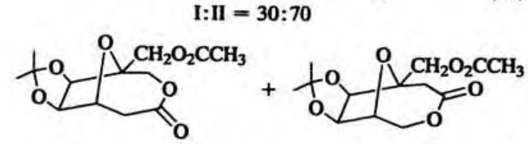
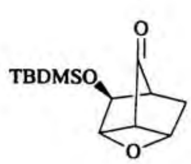
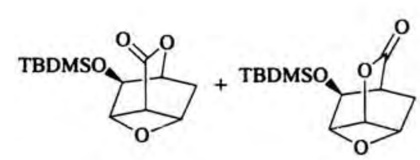
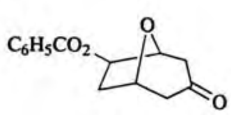
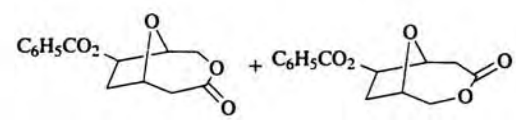
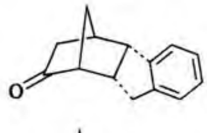
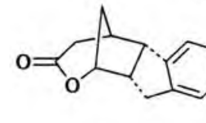
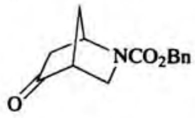
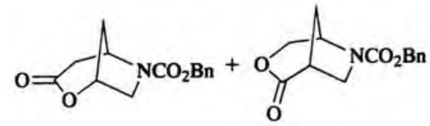
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I II (98) I:II = 23:77	38
	30% H_2O_2, NaOH, CH_3OH–H_2O, 0–20°	 (73)	409
	MCPBA, CH_2Cl_2, 8 h, reflux	(0)	453
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 15°	 I II (93) I:II = 30:70	38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I II (80) I:II = 35:65	38
	MCPBA, Na_2CO_3, CH_2Cl_2, 0–6°	 I II I:II = 90:10 (92)	373
C_{14}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 15°	 I II (95) I:II = 35:65	38
	MCPBA, TsOH, CH_2Cl_2, 40 h, 25°	 (88)	625
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 67:33 (49)	1073
	28% PAA, NaOAc, AcOH, 24 h, 25°	I:II = 100:0 (29)	1073

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

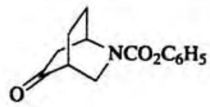
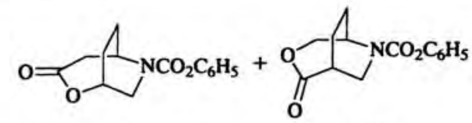
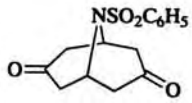
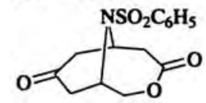
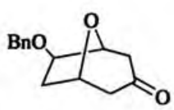
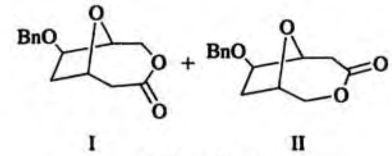
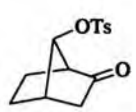
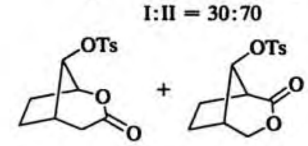
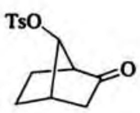
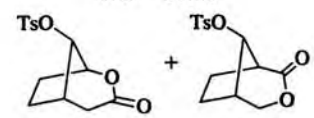
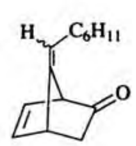
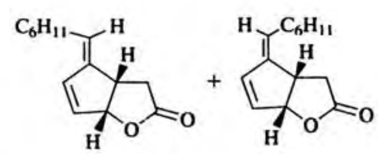
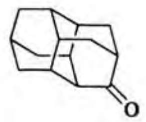
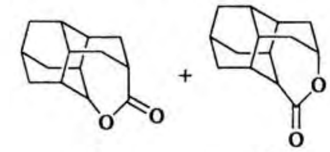
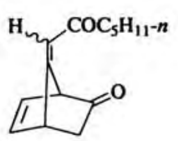
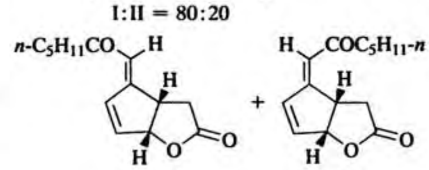
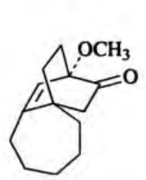
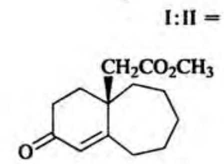
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 60:40	(51)	424
	PAA, NaOAc, AcOH, 24 h, 25°	I:II = 100:0	(51)	424
	MCPBA, CH_2Cl_2, 44 h, reflux		(68)	469, 1081
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 15°	 I II I:II = 30:70	(81)	38
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 60:40	(90)	369
	MCPBA, $NaHCO_3$, CH_2Cl_2, 48 h, 25°	 I II I:II = 60:40	(95)	369
	40% PAA, NaOAc, AcOH, CH_2Cl_2, 0–20°	 I II I:II = 32:68	(30)	409
	40% PAA, NaOAc, AcOH, 12 h, 25°	 I II I:II = 80:20	(97)	1082
	40% PAA, NaOAc, AcOH, CH_2Cl_2, 0–20°	 I II I:II = 33:67	(66)	409
	1. 40% PAA (1 eq), NaOAc, AcOH, 4 h, 50° 2. 40% PAA (1 eq), 48 h, 25° 3. K_2CO_3, $(CH_3)_2SO_4$, acetone, 2 h, reflux		(65)	753

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

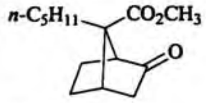
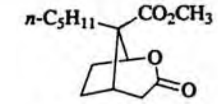
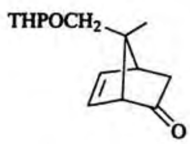
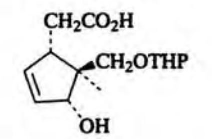
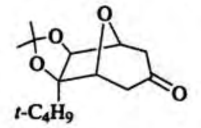
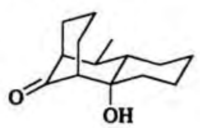
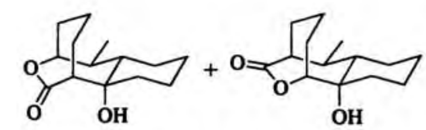
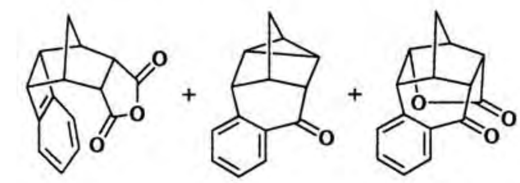
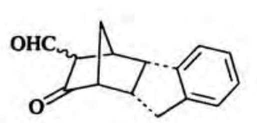
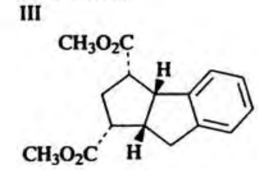
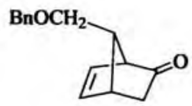
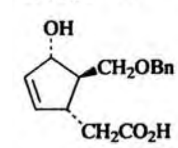
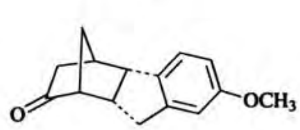
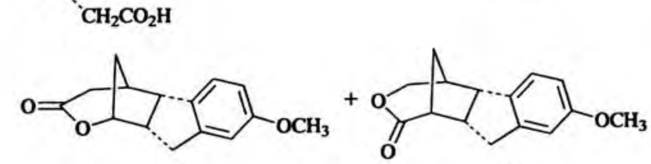
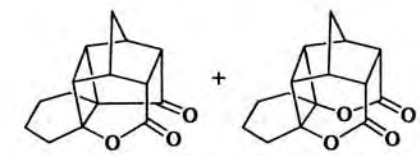
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PAA, AcOH		(94)	358
	30% H_2O_2, NaOH, CH_3OH–H_2O, 30 h, 5°		(89)	396, 401, 403
	TFPAA, Na_2HPO_4, CH_2Cl_2, 36 h, 20°		(0)	38
	—	 I II I:II = 60:40	(60)	475
C_{15}				
	$Pb(OAc)_4$, C_6H_6, C_5H_5N, 2 h	 I (65) II (15) III (10)		690
	CAN, CH_3CN–H_2O, 1 h, 0°	I (30) + II (40)		688
	19% PAA, NaOAc, AcOH, 24 h, 25°	III	(43)	440
	1. 30% H_2O_2, NaOH, 25° 2. CH_2N_2		(50)	625
	MCPBA, $NaHCO_3$, CH_2Cl_2, 0–10°		(40–50)	395
	MCPBA, $NaHCO_3$, CH_2Cl_2, 30 h, 25°	 I major II minor	(75)	1083
	MCPBA (2.5 eq), TsOH, benzene, 8 h, 25°	 I (51) II (36)		440
	MCPBA (5 eq), TsOH, benzene, 8 h, 25°	II	(73)	440

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

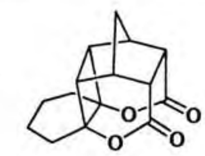
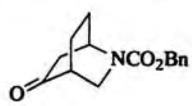
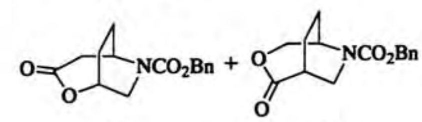
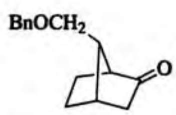
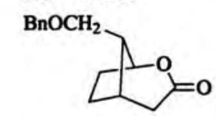
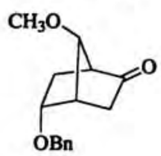
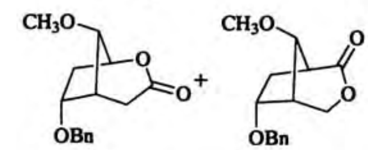
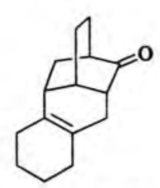
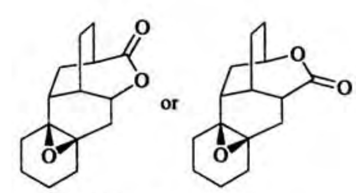
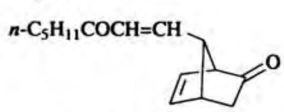
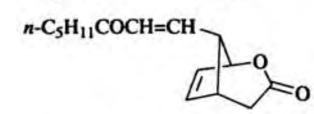
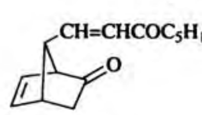
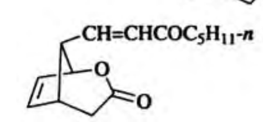
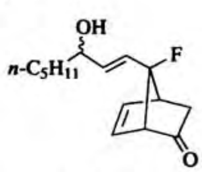
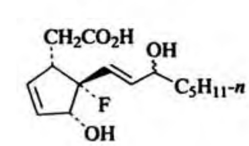
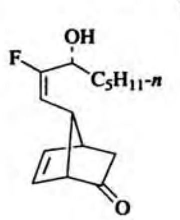
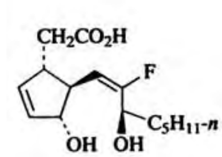
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA (2.5 eq), TsOH, benzene, 4 h, 25°		(48)	440
	MCPBA, $NaHCO_3$, CH_2Cl_2, 42 h, 25°	 I II I:II = 69:31	(80)	424
	28% PAA, NaOAc, AcOH, 18 h, 25°	I:II = 100:0	(82)	424
	MCPBA, CH_2Cl_2		(95)	348
	MCPBA, $NaHCO_3$, CH_2Cl_2, 25°	 I II I:II = 55:45	(81)	349
	30% H_2O_2, NaOAc, AcOH, 30 h, 50°	I:II = 100:0	(70)	349
	MCPBA, $NaHCO_3$, CH_2Cl_2, 9 h, 25°		(79)	421
	MCPBA, CH_2Cl_2, 25°		(62)	407
	MCPBA, CH_2Cl_2, 25°		(11)	407
	30% H_2O_2, NaOH, CH_3OH–H_2O, 48 h, 5°		(75)	398, 411
	30% H_2O_2, NaOH, CH_3OH–H_2O, 20 h, 0–5°		(75)	399

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

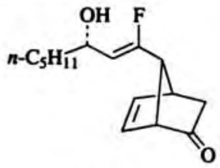
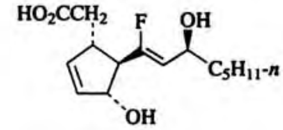
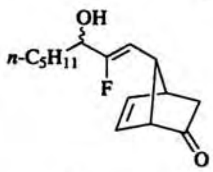
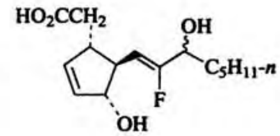
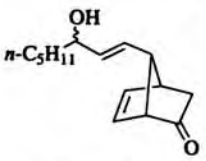
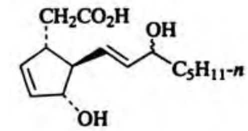
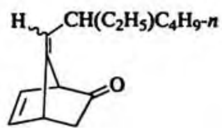
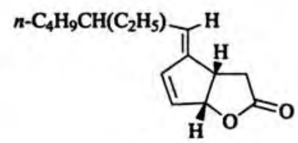
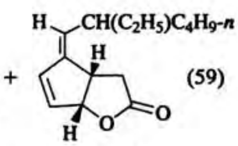
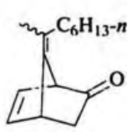
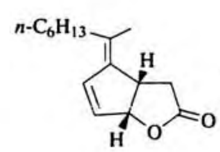
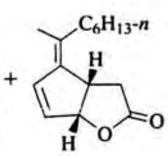
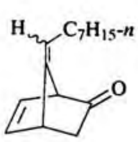
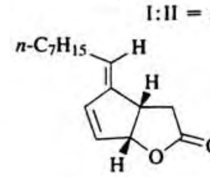
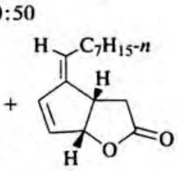
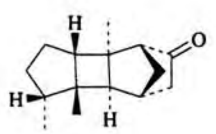
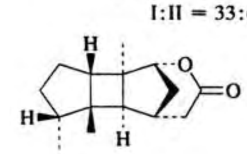
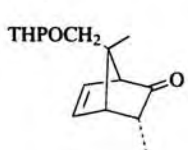
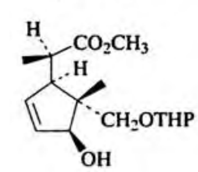
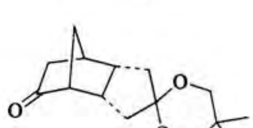
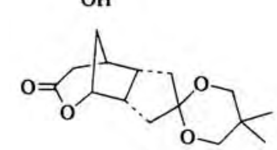
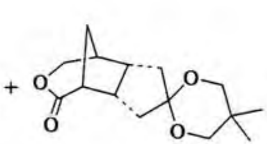
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 30% H_2O_2, NaOH, CH_3OH–H_2O, 20 h, 5° 2. 6 h, 25°	 (>53)	400
	30% H_2O_2, NaOH, CH_3OH–H_2O, 20 h, 5°	 (79)	399
	H_2O_2, NaOH	 (>79)	1084
	40% PAA, NaOAc, AcOH, CH_2Cl_2, 0–20°	 I +  II (59) I:II = 30:70	409
	30% H_2O_2, NaOH, CH_3OH–H_2O, 0–20°	 I +  II (69) I:II = 50:50	409
	30% H_2O_2, NaOH, CH_3OH–H_2O, 0–20°	 I +  II (63) I:II = 33:67	409
	PAA, AcOH	 (>76)	357
	30% H_2O_2, NaOH, CH_3OH–H_2O, 48 h, 0–5°	 (93)	405
	MCPBA, Na_2CO_3, CCl_4, 45 h, 25°	 I +  II (100) I:II = 73:27	334

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

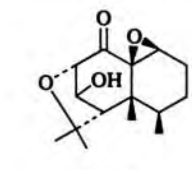
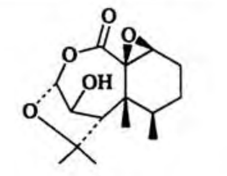
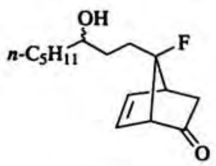
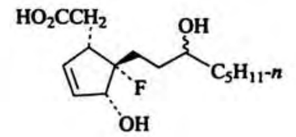
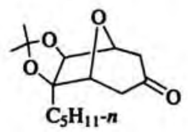
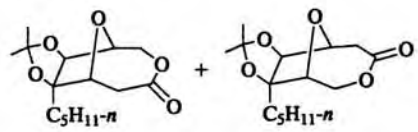
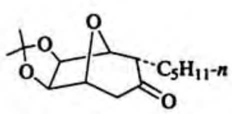
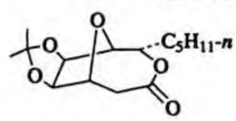
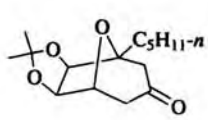
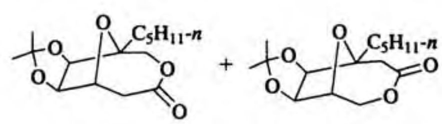
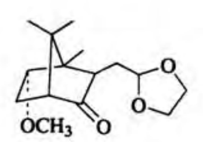
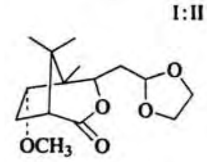
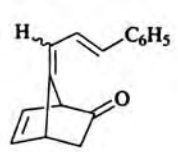
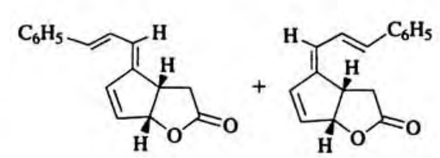
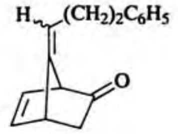
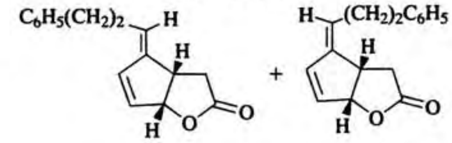
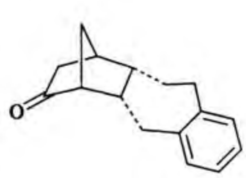
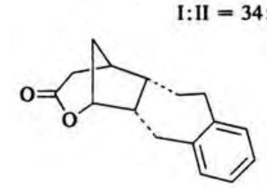
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, NaOH, $CH_3OH–H_2O$, 4 h, 25°		(—)	433
	1. 30% H_2O_2, NaOH, $CH_3OH–H_2O$, 3 h, 0° 2. 9 h, 25°		(100)	404
	TFPAA, Na_2HPO_4, CH_2Cl_2, 15 h, 20°	 I II I:II = 75:25	(85)	38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 8 h, 25°		(78)	38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 15 h, 20°	 I II I:II = 50:50	(80–100)	38, 39
	9% PAA, NaOAc, AcOH, 24 h, 25°		(31) (57)*	368
C_{16}				
	30% H_2O_2, NaOH, $CH_3OH–H_2O$, 0–20°	 I II I:II = 21:79	(29)	409
	30% H_2O_2, NaOH, $CH_3OH–H_2O$, 0–20°	 I II I:II = 34:66	(76)	409
	MCPBA, TsOH, CH_2Cl_2, 48 h, 25°		(91)	625

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

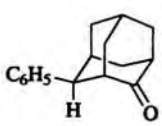
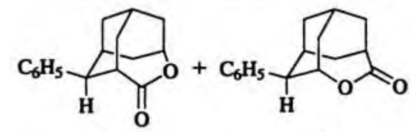
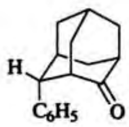
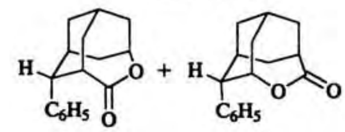
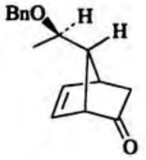
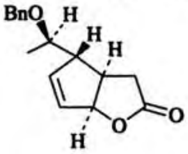
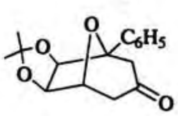
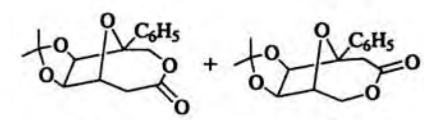
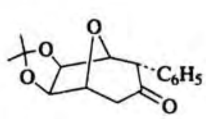
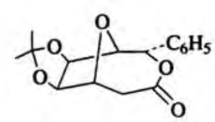
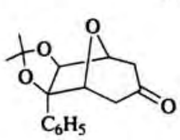
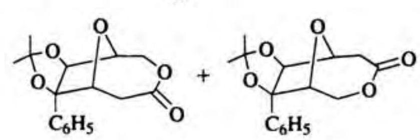
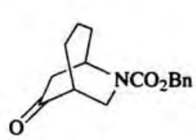
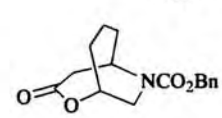
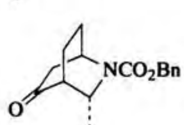
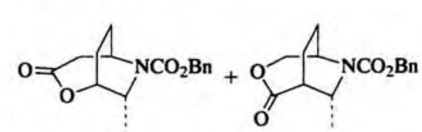
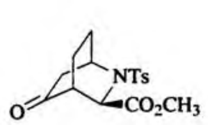
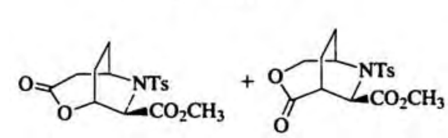
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2O_2, Ac_2O, AcOH, 10 h, 20°	 I + II; I:II = 67:33	(69)	476
	H_2O_2, Ac_2O, AcOH, 24 h, 50°	 I + II; I:II = 50:50	(76)	476
	1. 30% H_2O_2, NaOH, CH_3OH–H_2O, 48 h, 0° 2. BF_3 etherate/CH_2Cl_2, 45 min, 0°		(78)	418
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I + II; I:II = 88:12	(93)	38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 11 h, 25°		(67)	38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 36 h, 20°	 I + II; I:II = 61:39	(16) (81)*	38, 40
	TFPAA, Na_2HPO_4, CH_2Cl_2, 24 h, 25°		(61)	1073
	MCPBA, $NaHCO_3$, CH_2Cl_2, 64 h, 25°	 I + II; I:II = 81:19	(71)	424
	PAA, NaOAc, AcOH, 7 d, 25°		(0)	424
	PAA, NaOAc, AcOH, 72 h, 50°	 I + II; I:II = 96:4	(47)	427

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

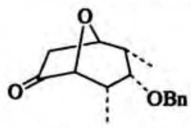
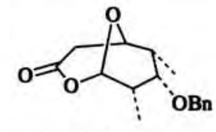
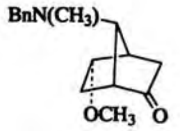
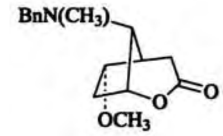
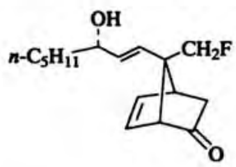
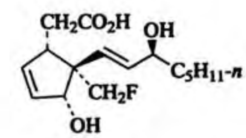
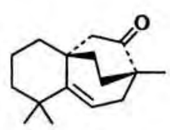
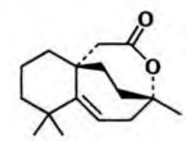
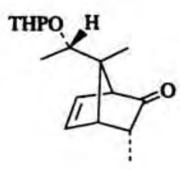
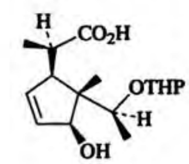
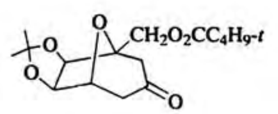
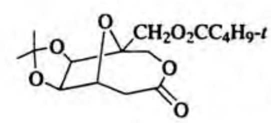
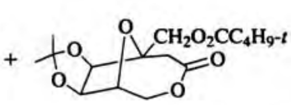
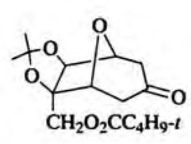
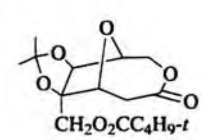
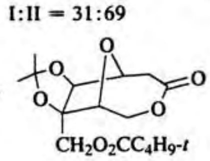
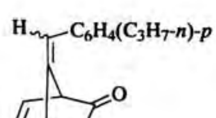
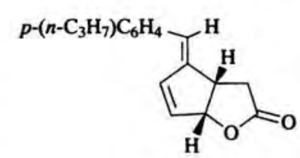
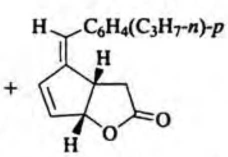
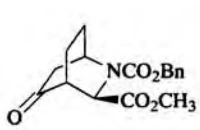
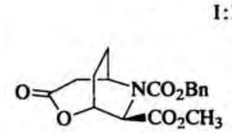
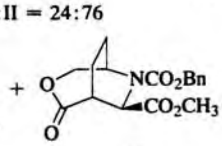
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2	 (80)	443
	40% PAA, CH_2Cl_2, 24 h, 25°	 (46)	347
	30% H_2O_2, NaOH, CH_3OH–H_2O, 36 h, 5°	 (81)	397
	$(CH_3)_3SiOOSi(CH_3)_3$, BF_3 etherate, CH_2Cl_2, 1 h, −20 to −10°	 (43)	477
	30% H_2O_2, NaOH, CH_3OH–H_2O, 48 h, 0°	 (75)	262, 415
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I +  II (91) I:II = 31:69	38, 39
	TFPAA, Na_2HPO_4, CH_2Cl_2, 36 h, 20°	 I +  II (38) (54)* I:II = 66:34	38
C_{17} 	30% H_2O_2, NaOH, CH_3OH–H_2O, 0–20°	 I +  II (72) I:II = 24:76	409
	MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°	 I +  II (59) I:II = 18:82	424, 426
	PAA, NaOAc, AcOH, 72 h, 25°	I:II = 100:0 (38)	424

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

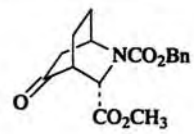
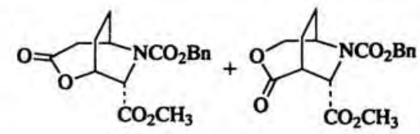
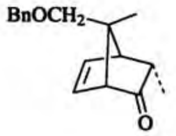
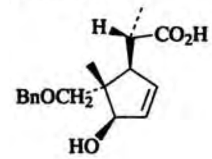
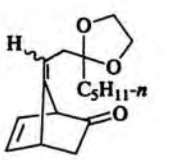
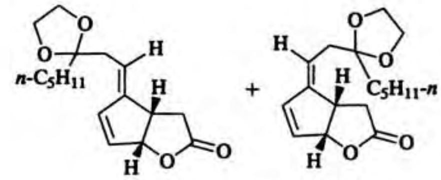
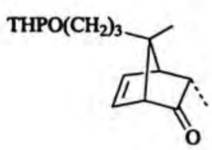
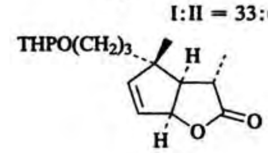
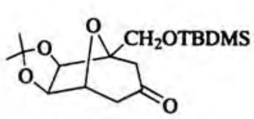
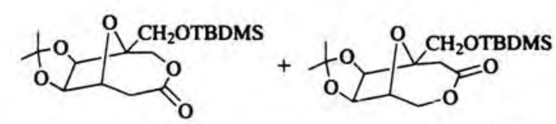
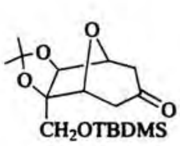
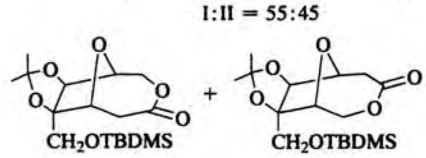
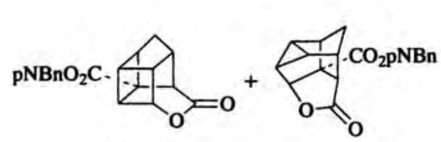
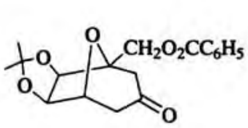
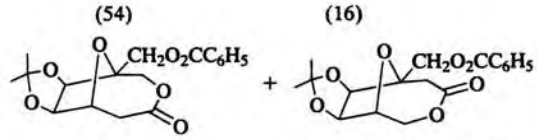
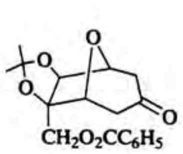
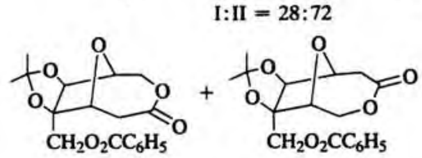
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°	 I + II; I:II = 38:62	(85)	424
	PAA, NaOAc, AcOH, 7 d, 25°	I:II = 66:34	(54)	424
	H_2O_2, NaOH, THF–CH_3OH–H_2O		(85)	414
	30% H_2O_2, NaOH, ether–H_2O, 0–20°	 I + II; I:II = 33:67	(80)	409
	1. H_2O_2, NaOH, CH_3OH–H_2O, 25° 2. TsOH, benzene, 25°		(79)	60
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I + II; I:II = 55:45	(100)	458
	TFPAA, Na_2HPO_4, CH_2Cl_2, 36 h, 20°	 I + II; I:II = 74:26	(36) (62)*	38, 40
C_{18}				
	85% MCPBA, $CHCl_3$, 2 h, 25°	 (54) + (16)		377
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I + II (100); I:II = 28:72		38
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 20°	 I + II; I:II = 60:40	(21) (72)*	38, 40

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

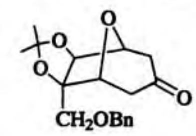
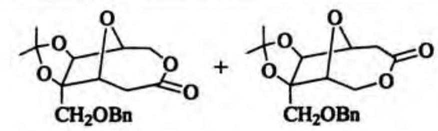
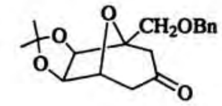
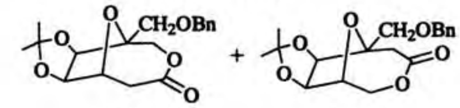
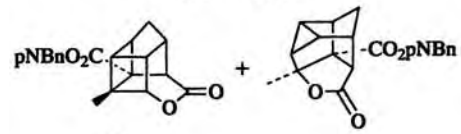
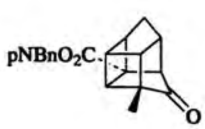
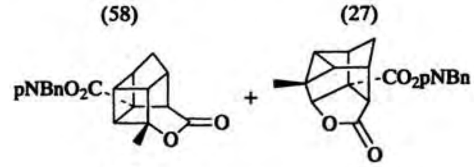
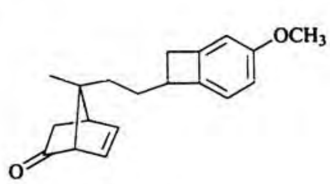
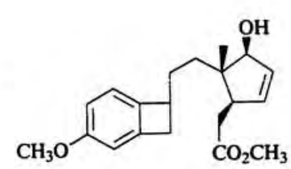
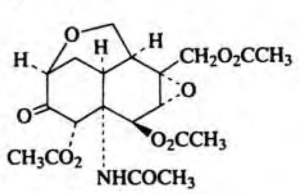
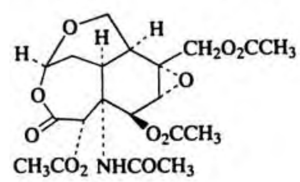
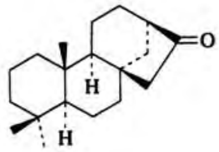
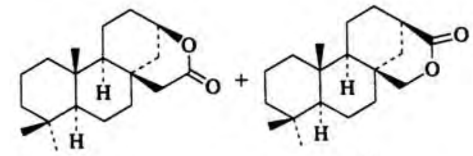
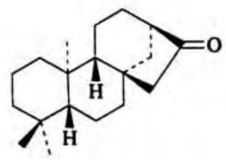
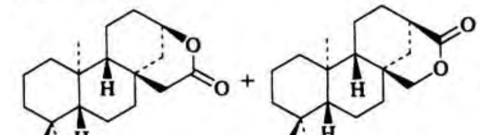
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 20°	 I + II (24) (68)* I:II = 77:23	38, 40
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	 I + II (83) I:II = 48:52	38
	85% MCPBA, $CHCl_3$, 2 h, 25°	 (58) + (27)	377
	85% MCPBA, $CHCl_3$, 3 h, 25°	 (76) + (11)	377
C_{19}			
	1. 30% H_2O_2, NaOH, CH_3OH–THF–H_2O, 12 h, 25° 2. CH_2N_2	 (84)	413
	MCPBA, CH_2Cl_2	 (100)	432
	TFPAA (90%), CH_2Cl_2, 4 h, heat	 I + II (—) I major, II trace	436
	TFPAA (90%), CH_2Cl_2, 1 h, heat	I:II = 100:0 (67)	435
	TFPAA (90%), CH_2Cl_2, 4 h, heat	 I + II (—) I major, II trace	436

TABLE IV. Reactions of Bridged Bicyclic and Polycyclic Ketones (*Continued*)

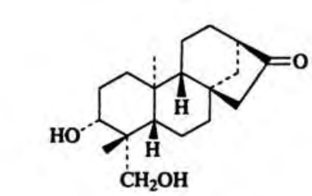
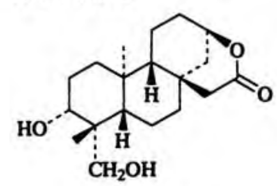
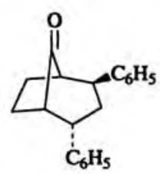
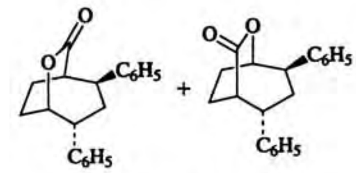
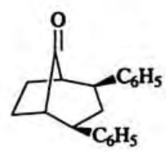
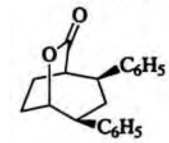
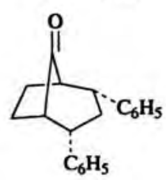
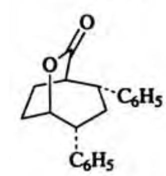
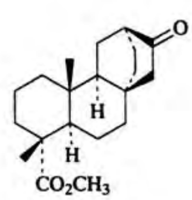
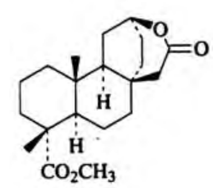
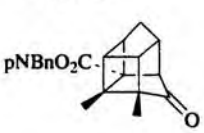
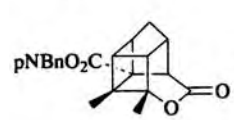
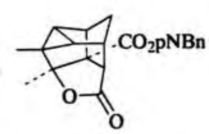
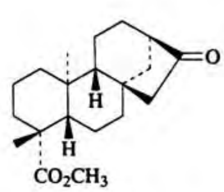
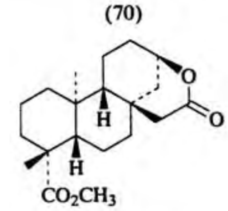
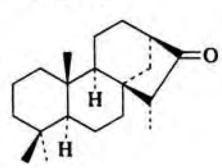
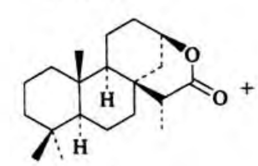
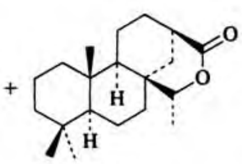
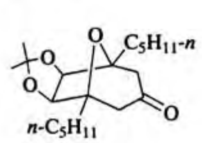
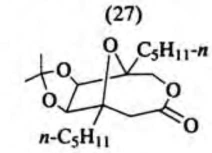
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA (85%), CH_2Cl_2, 12 h, 20°	I:II = 100:0 (48)	435
	PBA, TsOH, $CHCl_3$, 3 d, 0°	 (72)	434
C_{20}			
	40% PAA, NaOAc, AcOH, 5 d, 25°	 I + II; 60:40 ratio of isomers (95)	474
	40% PAA, NaOAc, AcOH, 5 d, 25°	 (100)	474
	30% H_2O_2, 40% H_2SeO_4, THF, 25 h, reflux	 (89)	474
	MCPBA, $CHCl_3$, 18 h, heat	 (60)	419
	85% MCPBA, $CHCl_3$, 2 h, 25°	 (70) +  (13)	377
	PBA, TsOH, $CHCl_3$	 (76)	434
	TFPAA (95%), CH_2Cl_2, 4 h, reflux	 (27) +  (52) (20)*	436
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 20°	 (77) +(12)*	452, 454

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

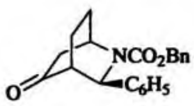
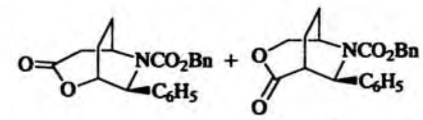
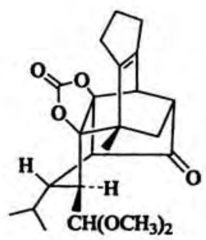
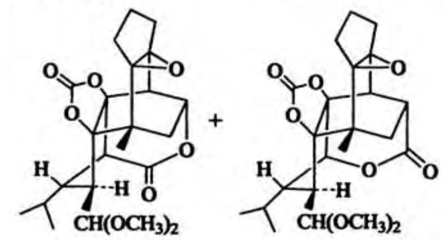
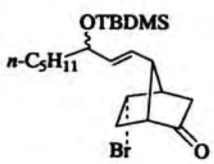
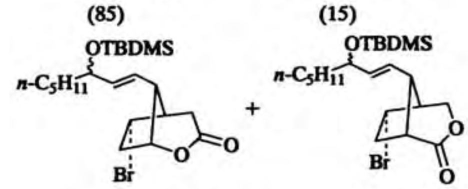
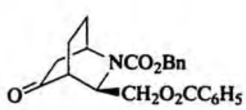
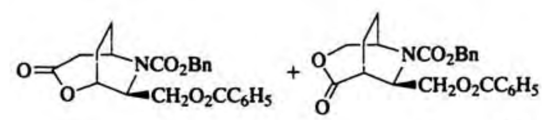
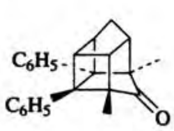
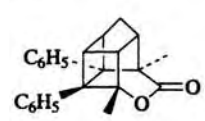
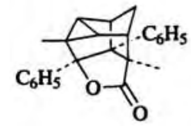
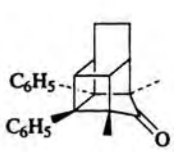
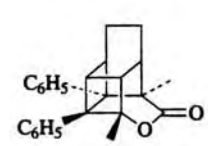
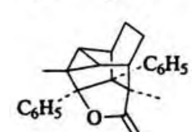
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{21}				
	MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°	 I II; I:II = 60:40	(55)	424
	PAA, NaOAc, AcOH, 24 h, 25°	I:II = 100:0	(38)	424
	1. 40% PAA, NaOAc, AcOH, 15 h, 25° 2. 1 h, 80°	 (85) (15)		441
	MCPBA, $NaHCO_3$, $CHCl_3$, 16 h, 25°	 I II; I:II = 75:25	(95)	341, 342
C_{23}				
	PAA, NaOAc, AcOH, 48 h, 25°	 I II (68); I:II = 84:16		424, 426
	MCPBA, $NaHCO_3$, CH_2Cl_2, 72 h, 25°	I:II = 60:40	(42)	424, 426
C_{24}				
	H_2O_2, AcOH		(51)	379
	H_2O_2, AcOH, heat		(21)	379
C_{25}				
	H_2O_2, AcOH		(36)	379
	H_2O_2, AcOH, heat		(26)	379

TABLE IV. REACTIONS OF BRIDGED BICYCLIC AND POLYCYCLIC KETONES (*Continued*)

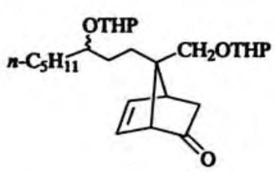
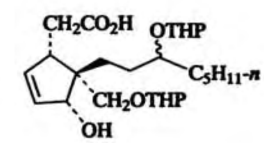
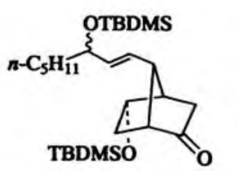
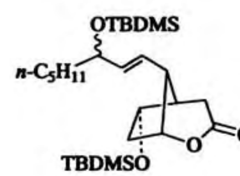
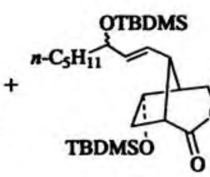
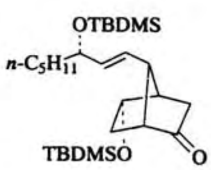
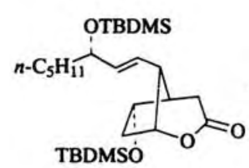
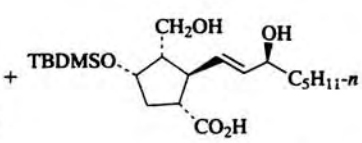
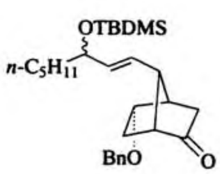
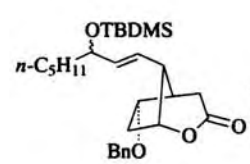
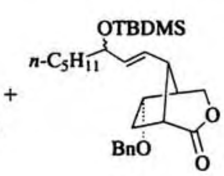
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}			
	30% H_2O_2, NaOH, CH_3OH–H_2O, 5 d, 5°	 (85)	402
C_{27}			
	40% PAA, NaOAc, AcOH–CH_2Cl_2, 4 d, −20°	 (80) +  (20) (100)	333, 336, 338, 345, 349, 350
	1. PAA, AcOH 2. NaOH	 (70) +  (14)	332, 339
C_{28}			
	40% PAA, NaOAc, CH_2Cl_2	 I +  II (74) I:II = 70:30	351

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES

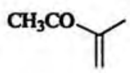
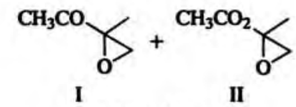
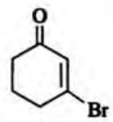
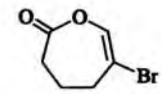
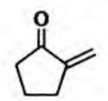
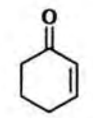
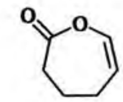
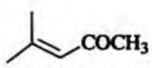
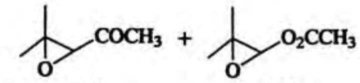
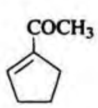
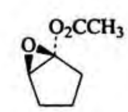
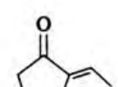
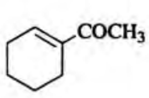
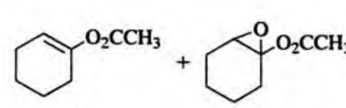
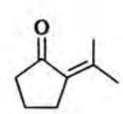
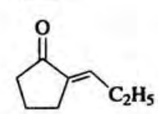
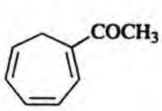
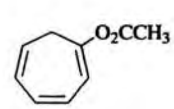
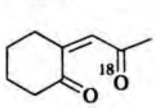
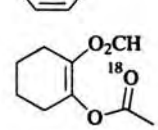
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	45% PAA, $CHCl_3$, 5 d, 25°	 I:II = 89:11 (22)	480
C_6			
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, 4 h, 0°	 (68)	493
	15% H_2O_2, NaOH, CH_3OH, 20 min, −10 to 25°	$CH_3CO(CH_2)_3CO_2H$ (I) (25) + $CH_3CO(CH_2)_3CO_2C_2H_5$ (II) (60)	179
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	I (33)	158
	MCPBA, CF_3CO_2H, CH_2Cl_2, 3 h, 0–25°	 (52)	742
	1. t-$C_4H_9(CH_3)_2SiCl$, LDA, THF–HMPA 2. H_2O_2 (anh), TFAA 3. $(C_6H_5CO)_2O$, p-dimethylaminopyridine, hexane, −20°	■ (70)	182, 1085
	45% PAA, $CHCl_3$, 4.5 h, 20–25°	 (20) + (53)	480
C_7			
	MCPBA, H_2SO_4, $CHCl_3$, 48 h, 0–20°	 (35) (60)*	488
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	$CH_3CH_2CO(CH_2)_3CO_2H$ (38)	158
C_8			
	MCPBA, H_2SO_4, $CHCl_3$, 48 h, 0–20°	 (42) + (5) (49)*	488
	15% H_2O_2, NaOH, C_2H_5OH, 20 min, −10 to 25°	i-$C_3H_7CO(CH_2)_3CO_2C_2H_5$ (60) + i-$C_3H_7CO(CH_2)_3CO_2H$ (25)	158, 179
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_3H_7CO(CH_2)_3CO_2H$ (36)	158
C_9			
	MCPBA, $NaHCO_3$, CH_2Cl_2, 15 h, 20°	 (53) (28)*	487
	80–85% MCPBA, CH_2Cl_2, 2 h, 25°	 (85)	654

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

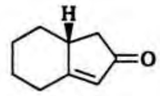
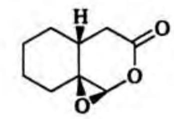
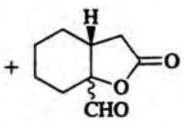
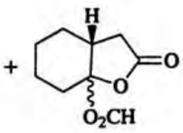
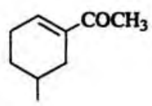
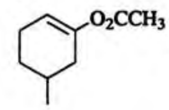
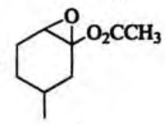
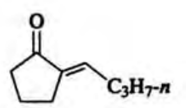
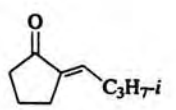
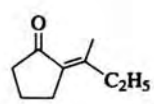
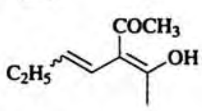
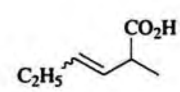
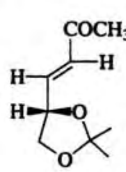
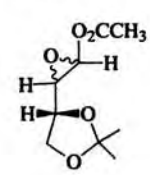
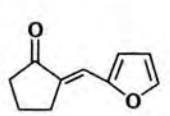
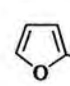
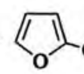
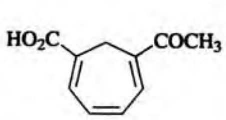
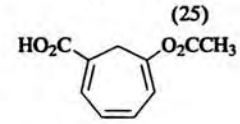
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, 90 h, 10°	 I (36) (64)*	298
	MCPBA (2 eq), CH_2Cl_2, 24 h, 25°	I (43) (57)*	298
	TFPAA, Na_2HPO_4, CH_2Cl_2, 24 h, 25°	I +  +  (70)* (9) (20) (1)	298
	MCPBA, H_2SO_4, $CHCl_3$, 48 h, −5°	 (50) +  (13) (38)*	488
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_4H_9CO(CH_2)_3CO_2H$ I (37)	158
	15% H_2O_2, NaOH, C_2H_5OH, 20 min, −10 to 25°	I (25) + n-$C_4H_9CO(CH_2)_3CO_2C_2H_5$ (60)	179
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	i-$C_4H_9CO(CH_2)_3CO_2H$ (44)	158
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	s-$C_4H_9CO(CH_2)_3CO_2H$ (25)	158
	50% H_2O_2, NaOH, CH_3OH, 1.25 h, 38–40°	 (70)	677
	MCPBA, CH_2Cl_2, 10 d, 25°	 (19) (56)*	482
C_{10}			
	15% H_2O_2, NaOH, C_2H_5OH, 20 min, −10 to 25°	 $CH_2CO(CH_2)_3CO_2C_2H_5$ (60) +  $CH_2CO(CH_2)_3CO_2H$ (25)	179
	80% MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h, 15–30°	 (71)	487

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

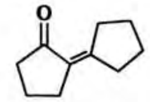
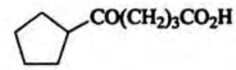
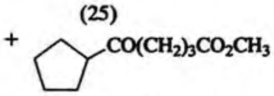
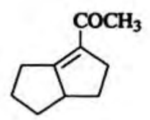
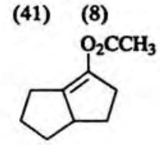
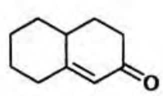
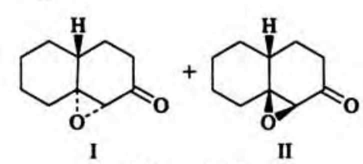
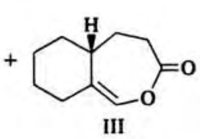
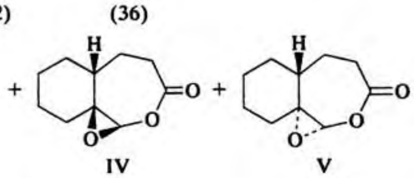
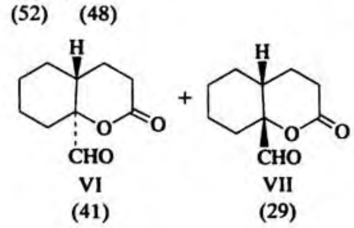
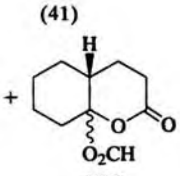
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	15% H_2O_2, NaOH, CH_3OH, 20 min, −10 to 25°	 I (25) +  II (60) + $HO_2C(CH_2)_3CO_2H$ III (—)	179
	1. 30% H_2O_2, $NaHCO_3$, CH_3OH, 32 h, 25° 2. 3 h, 70°	I (22) (55)*	179
	$K_2S_2O_8$, H_2SO_4	I + III (41) (8)	179
	MCPBA	 (—)	489
	H_2O_2, NaOH, 40°	 (72) I:II = 10:90	298
	85% MCPBA (1 eq), CH_2Cl_2, 24 h, −7°	II +  (30)* III (2) (36) +  IV (16), V (16)	298
	85% MCPBA (2 eq), CH_2Cl_2, 24 h, 25°	IV + V (52) (48)	298
	TFPAA (90%) (3 eq), Na_2HPO_4, CH_2Cl_2, 72 h, 10°	 VI (41), VII (29) +  VIII (30)	298
	TFPAA (90%) (3 eq), Na_2HPO_4, CH_2Cl_2, 72 h, 25°	IV + VII + VIII (24) (10) (66)	298

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

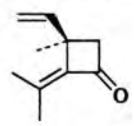
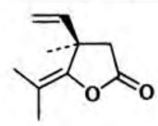
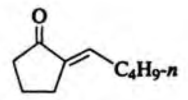
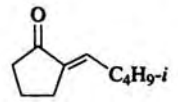
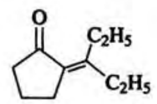
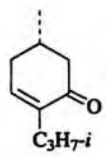
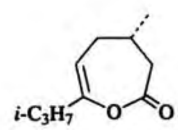
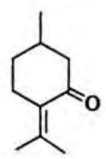
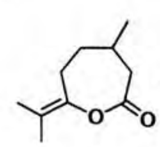
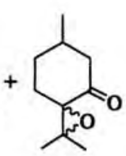
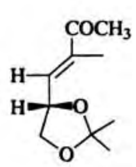
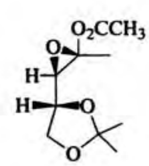
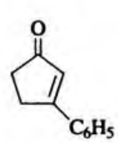
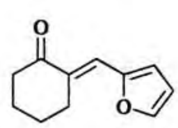
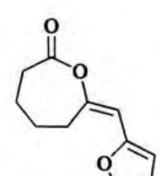
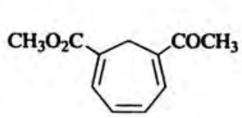
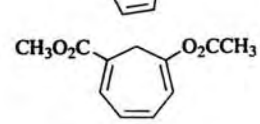
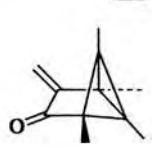
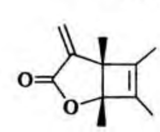
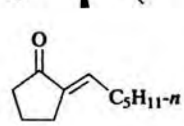
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	40% PAA, KOAc, AcOH, 25°	 (60)	106
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_5H_{11}CO(CH_2)_3CO_2H$ (29)	158
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	i-$C_4H_9CH_2CO(CH_2)_3CO_2H$ (30)	158
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	$(C_2H_5)_2CHCO(CH_2)_3CO_2H$ (24)	158
	—	 (74)	492
	40% PAA, KOAc, AcOH	 (40) +  (—)	106
	MCPBA, CH_2Cl_2, 3 d, 25°	 (59)	481
C_{11}			
	PBA, $CHCl_3$, 28°	$C_6H_5CO_2C_2H_5$ (50) + $C_6H_5CO(CH_2)_2CO_2H$ (5)	1086
	40% PAA, KOAc, AcOH, 70 min, 30°	 (60–80)	491
	80% MCPBA, $NaHCO_3$, CH_2Cl_2, 2 d, 20°	 (51)	487
	MCPBA, $CHCl_3$, 25°	 (—)	490
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_6H_{13}CO(CH_2)_3CO_2H$ (39)	158

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

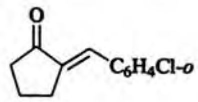
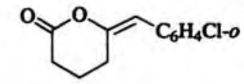
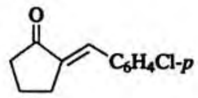
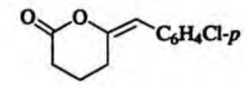
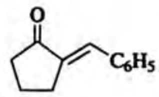
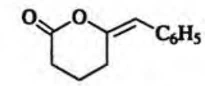
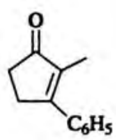
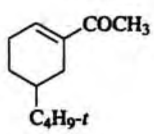
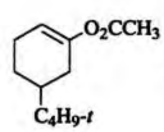
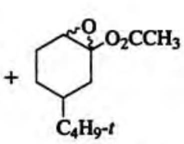
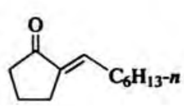
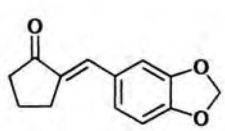
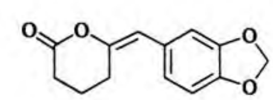
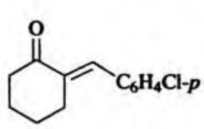
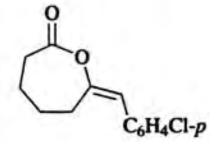
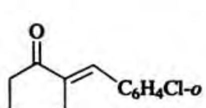
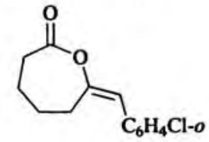
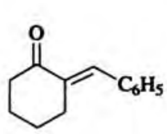
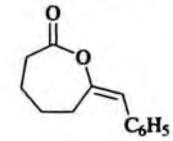
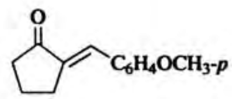
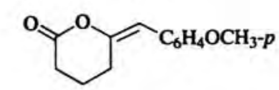
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{12}				
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	PAA, KOAc, AcOH, 70 min, 30°		(62)	491
	15% H_2O_2, NaOH, C_2H_5OH, 20 min, −10 to 25°	$C_6H_5CH_2CO(CH_2)_3CO_2C_2H_5$ (60) + $C_6H_5CH_2CO(CH_2)_3CO_2H$ (25)		158, 179
	30% H_2O_2, NaOH, CH_3OH, 4 h, 25°	$C_6H_5COCH_2CH_2OH$	(58)	494
	MCPBA, H_2SO_4, $CHCl_3$, 48 h, −5°	 (51) +  (10)	(35)[a]	488
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_7H_{15}CO(CH_2)_3CO_2H$	(36)	158
C_{13}				
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°		(60–80)	491

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

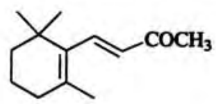
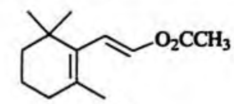
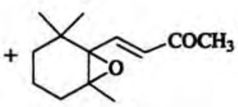
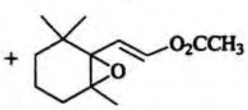
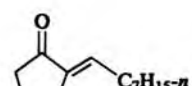
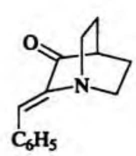
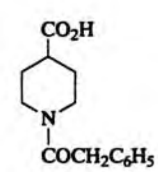
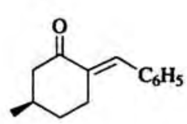
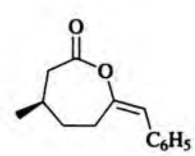
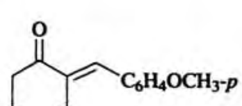
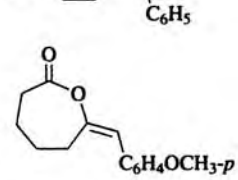
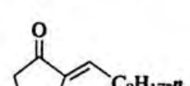
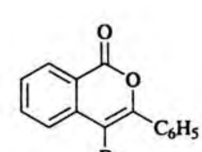
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	3-Heptadecylmonoperphthalic acid, $NaHCO_3$, hexane-H_2O (1:10), 24 h, 25°	 I +  II +  III; I:II:III = 83:11:6 (68) (30)*	484
	PBA (2 eq.)	III (100)	483, 484
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_8H_{17}CO(CH_2)_3CO_2H$ (28)	158
C_{14}			
	30% H_2O_2, NaOH, C_2H_5OH, 15 h, 5°	 (40)	520
	40% PAA, KOAc, AcOH, 70 min, 30°	 (60–80)	491
	40% PAA, KOAc, AcOH, 70 min, 30°	 (60–80)	491
	H_2O_2, NaOH, C_2H_5OH, −10 to 25°	n-$C_9H_{19}CO(CH_2)_3CO_2H$ (46)	158
C_{15}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 3 h, 0°	 (82)	493
$C_6H_5CH{=}CHCOC_6H_4F$-p	$K_2S_2O_8$, H_2SO_4, AcOH, 50 h, 17°	$C_6H_5CH{=}CHO_2CC_6H_4F$-p (37) (15)*	486
$C_6H_5CH{=}CHCOC_6H_5$	$K_2S_2O_8$, H_2SO_4, AcOH, 170 h, 17°	$C_6H_5CH{=}CHO_2CC_6H_5$ (20) (20)*	486
	PBA, $CHCl_3$, 45 h, 25°	C_6H_5CHO (69) + C_6H_5OH (21) + $C_6H_5CO_2H$ (69) (56)*	485

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

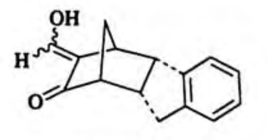
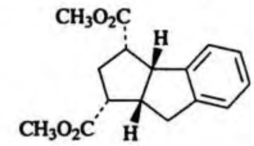
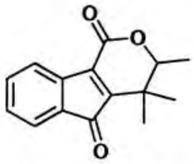
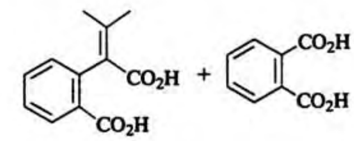
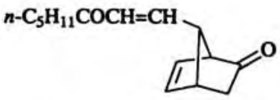
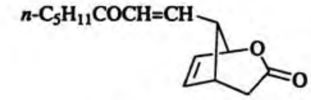
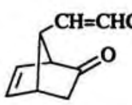
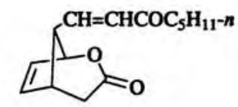
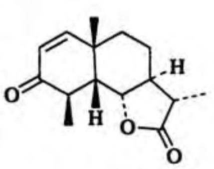
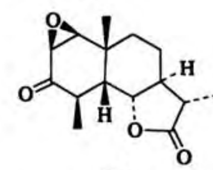
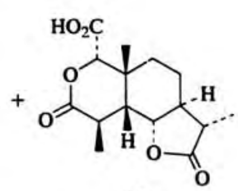
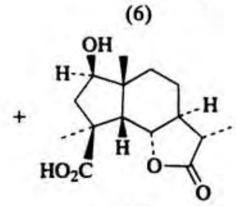
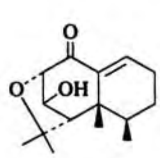
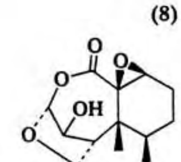
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 30% H_2O_2, NaOH, 25° 2. CH_2N_2	 (50)	625
	3% H_2O_2, NaOH	 (—)	674
	MCPBA, CH_2Cl_2, 25°	 (62)	407
	MCPBA, CH_2Cl_2, 25°	 (11)	407
	H_2O_2, Na_2CO_3, dioxane–H_2O, 60 h, 0°	 (66) +  (6) +  (8)	673
	30% H_2O_2, NaOH, CH_3OH–H_2O, 9 h, 15°	 (43)	433
C_{16}			
$C_6H_5CH{=}C(C_6H_5)COCH_3$	PBA, $CHCl_3$, 27°	$C_6H_5CO_2H$ (12) + C_6H_5CHO (3) + $C_6H_5COCHOHC_6H_5$ (14) + $C_6H_5COCH_2C_6H_5$ (71)	485
$C_6H_5CH{=}C(CH_3)COC_6H_5$	PBA, $CHCl_3$, 118 h, 25°	C_6H_5CHO (59) + $C_6H_5CO_2H$ (78) + C_6H_5OH (16) (55)*	485

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

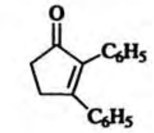
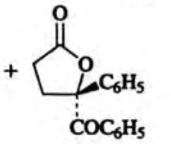
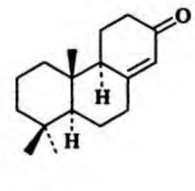
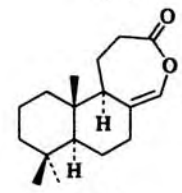
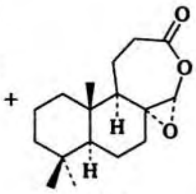
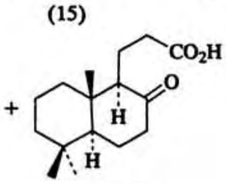
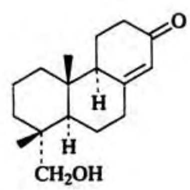
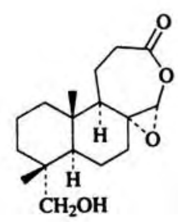
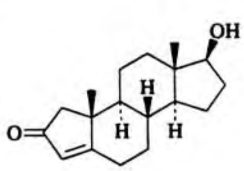
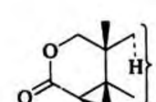
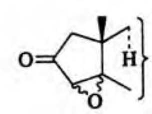
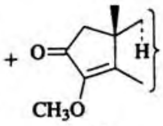
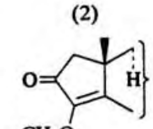
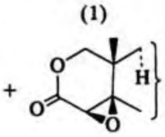
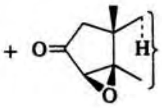
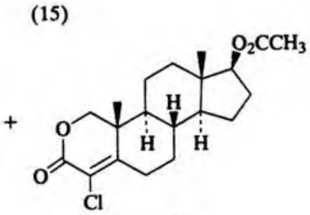
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	PBA, $CHCl_3$, 24 h, 28°	$HO_2C(CH_2)_2C(C_6H_5)OHCOC_6H_5$ (86) +  (12)	1086
	MCPBA, $NaHCO_3$, CH_2Cl_2, 24 h, 25°	 (15) +  (37) +  (8)	305
	MCPBA, CH_2Cl_2, 25°, 6 h	 (98)	1087
C_{18}			
	30% H_2O_2, NaOH, *t*-BuOH, 6 d, 25°	 I (40)	299
	30% H_2O_2, NaOH, CH_3OH, 16 h, 25°	 (2) +  (1) + I (6)	499
	1. 30% H_2O_2, NaOH, CH_3OH, 25° 2. AcOH, HCl	 (—) +  (15) +  (—) +  (5)	499

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

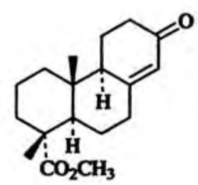
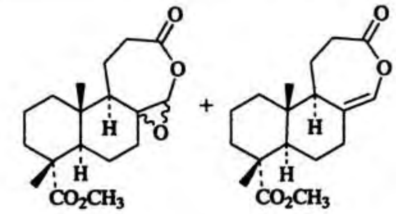
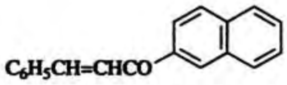
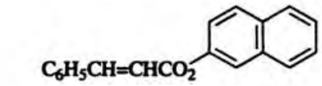
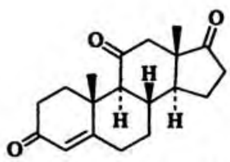
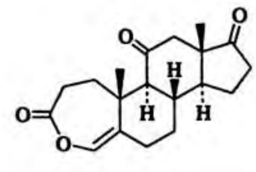
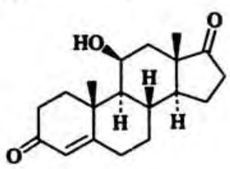
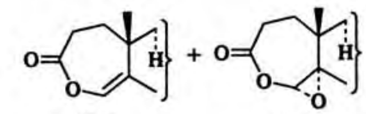
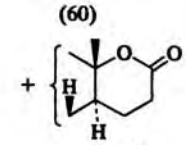
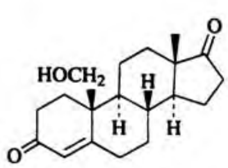
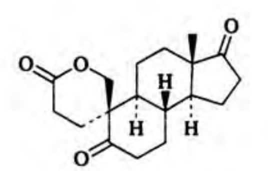
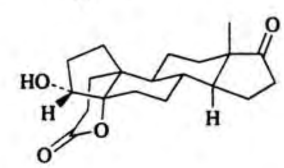
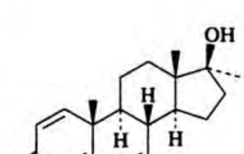
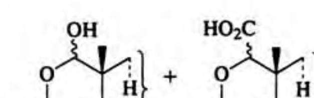
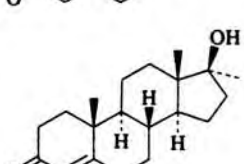
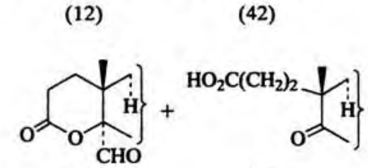
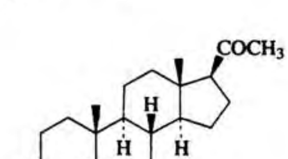
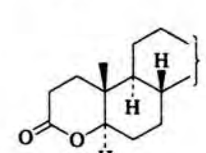
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. MCPBA (2 eq), CH_2Cl_2, 1–2 h, 25° 2. 5 h, reflux	 (43) (—)		496, 497
C_{19}				
	$K_2S_2O_8$, H_2SO_4, AcOH, 170 h, 17°		(25) (25)*	486
	PBA, $HClO_4$, $CHCl_3$, 16 h, 25°		(29) (10)*	281
	PBA, $HClO_4$, $CHCl_3$, 16 h, 25°	 (60) (8)  (trace)		281
	1. 30% H_2O_2, NaOH, CH_3OH, 15.5 h, 0–25° 2. HCl, H_2O		(26)	1088
	MCPBA, $CHCl_3$, 35% $HClO_4$, 2 d, 25°		(27) (13)*	1000
C_{20}				
	30% H_2O_2, NaOH, CH_3OH, 72 h, 25°	 (12) (42)		514
	TFPAA, Na_2HPO_4, $CHCl_3$, 1 h, 40–50°	 (18) (1)		509, 510
C_{21}				
	K_2SO_5, H_2SO_4, AcOH, 3 d		(21)	507

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

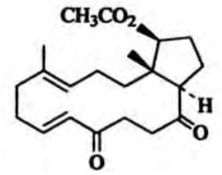
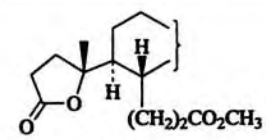
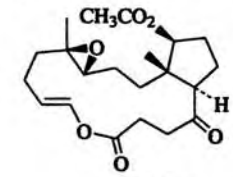
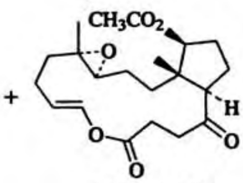
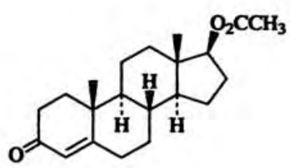
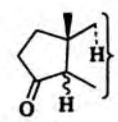
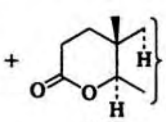
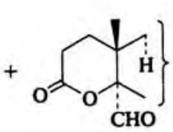
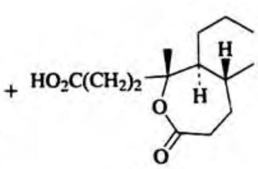
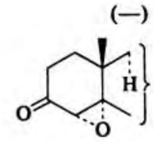
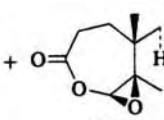
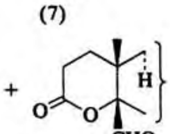
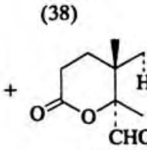
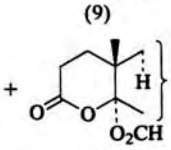
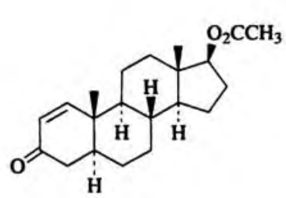
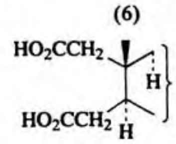
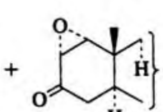
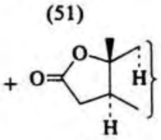
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 50% H_2O_2, SeO_2, *t*-BuOH, 7 h, reflux 2. CH_2N_2	 (33)	101
	MCPBA, $NaHCO_3$, CH_2Cl_2–ether, 25°	 I (67) +  II I:II = 45:55	519
	MCPBA (2 eq), $HClO_4$, $CHCl_3$, 12 h, 25°	 (4) +  (2) +  (—) +  (6)	508
	PBA (4 eq), $HClO_4$, $CHCl_3$, 84 h, 25°	 (7) +  (38) +  (9) +  (9) +  (6)	508
	50% H_2O_2, SeO_2, *t*-BuOH, 16 h, reflux	 (51) +  (4) +  (8)	505

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

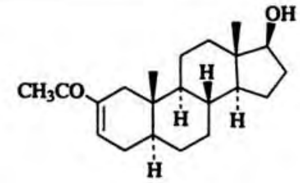
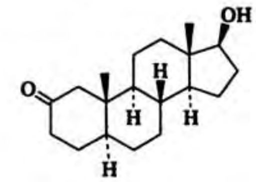
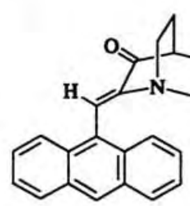
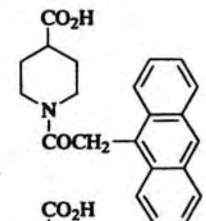
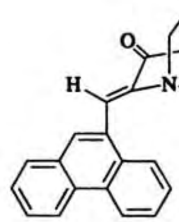
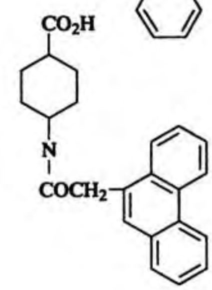
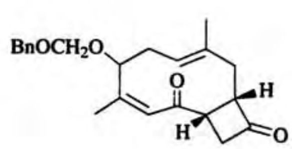
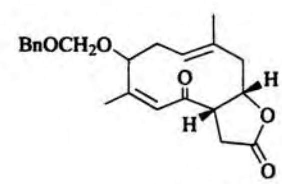
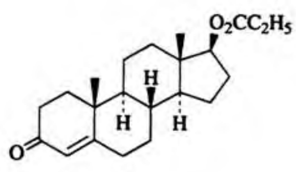
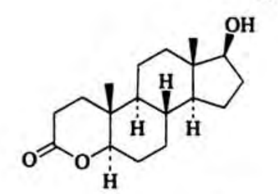
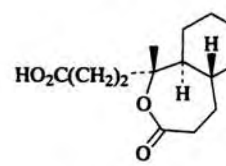
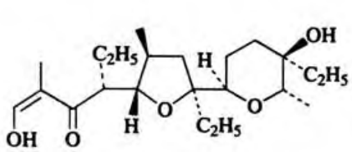
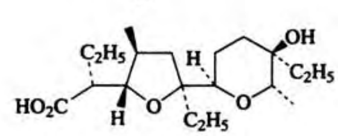
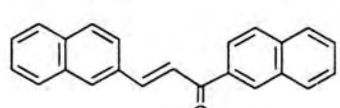
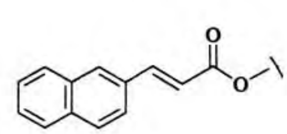
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, H_2SO_4, $CHCl_3$, 72 h, 25°	 (44) (36)*	488
C_{22}			
	30% H_2O_2, NaOH, C_2H_5OH, 40 h, 25°	 (82)	520
	30% H_2O_2, NaOH, C_2H_5OH, 15 h, 5°	 (60)	520
	H_2O_2 (anh), $Ti(OC_3H_7\text{-}i)_4$, ether, $(i\text{-}C_3H_7)_2NC_2H_5$, 15 min, −30°	 (55)	236
	1. K_2SO_5, H_2SO_4, AcOH, 7 d, 25° 2. Saponification	 (26)	507
	H_2O_2, SeO_2, $t\text{-}C_4H_9OH$	 (72)	101, 515
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, several min	 (79)	80
C_{23}			
	$K_2S_2O_8$, H_2SO_4, AcOH, 24 h, 17°	 (19) (30)*	486

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TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

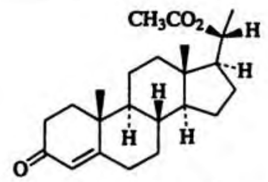
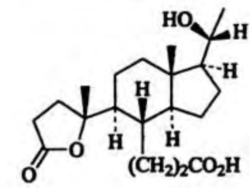
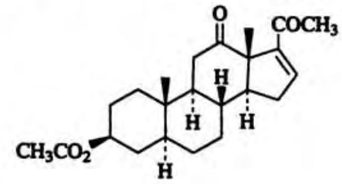
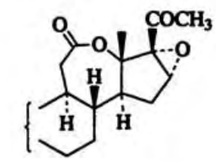
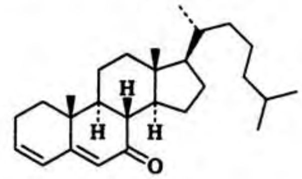
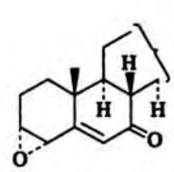
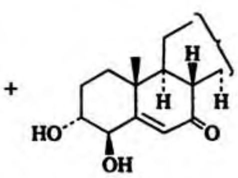
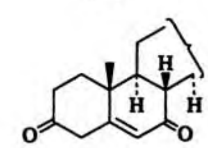
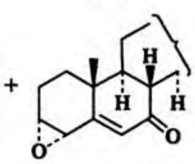
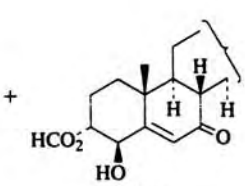
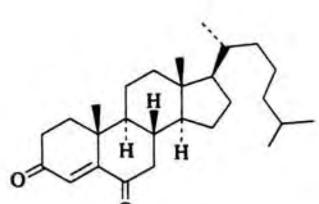
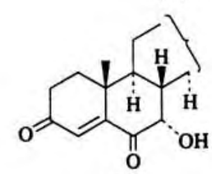
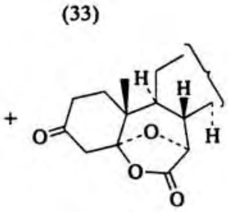
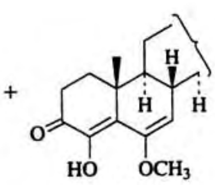
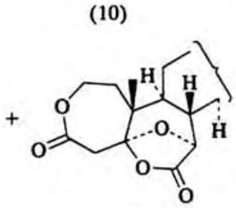
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, SeO_2, t-BuOH, 7 h, reflux	 (80)	101, 515
	PBA, H_2SO_4, AcOH, 14 d, 25°	 (16)	518
C_{27}			
	PBA (2.5 eq), TsOH, $CHCl_3$, 24 h, 25°	 (41) +  (11)	503
	30% H_2O_2, 98% HCO_2H, 3 h, 40°	 (10) +  (16)	503
		+  (23)	
	PBA (1 eq), TsOH, $CHCl_3$(CH_3OH trace), 60 h, 25°	 I (33) +  II (10) +  III (4)	(25)* 303
	PBA (2.5 eq), TsOH, $CHCl_3$, 96 h, 25°	II (38) +  IV (22)	(25)* 303

TABLE V. Reactions of α,β-Unsaturated Ketones (*Continued*)

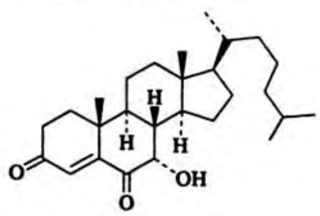
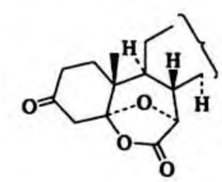
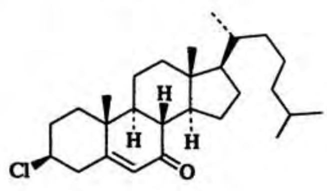
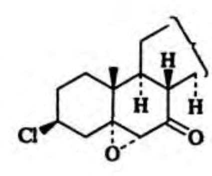
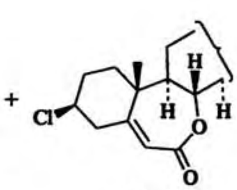
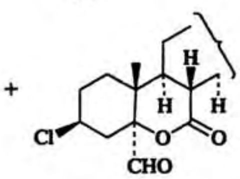
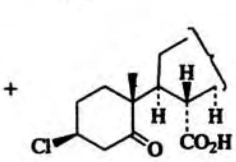
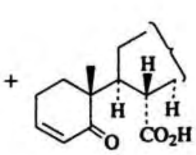
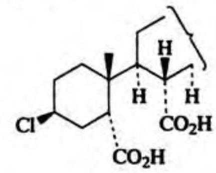
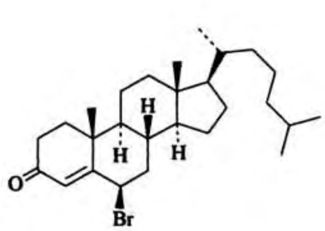
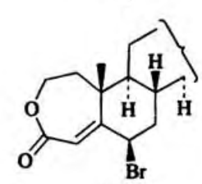
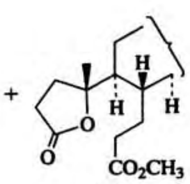
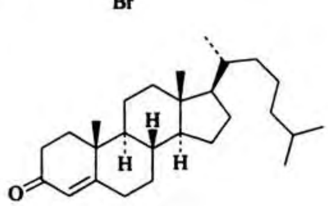
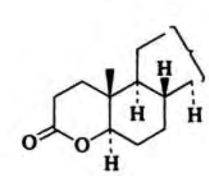
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 8 h, 25°	 (71)	303
	PBA (1–2 eq), TsOH, 140 h, 25°	 I (3) +  II (3) +  III (7) +  IV (8)	513
	PBA (3 eq), TsOH, $CHCl_3$, 8 h, 25°	I–IV (—) +  V (2)	513
	TFPAA, Na_2HPO_4, CH_2Cl_2, 75 min	 VI (—)	506
	PBA, TsOH, $CHCl_3$ (CH_3OH), 6 d, 25°	 (8) +  (19)	516
	K_2SO_5, H_2SO_4, AcOH, 7 d, 25°	 (35)	507

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

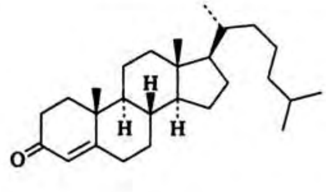
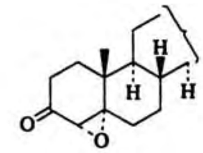
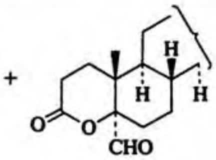
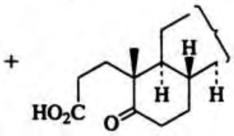
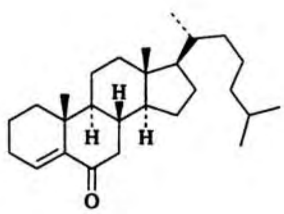
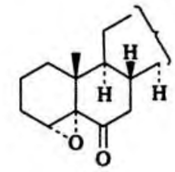
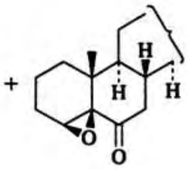
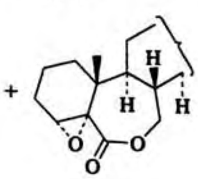
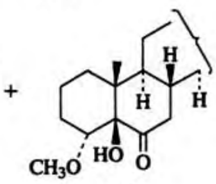
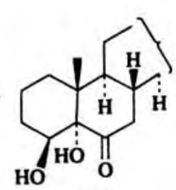
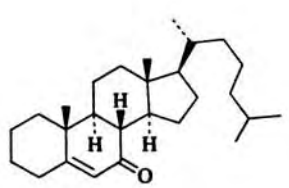
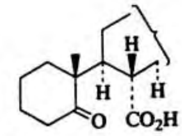
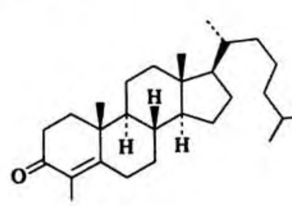
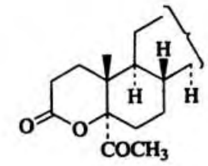
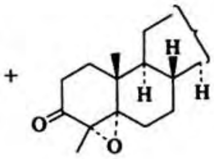
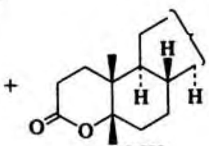
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h, 30–40°	 (5) +  (70) +  (2)	509, 510
	PBA (CH_3OH impurity), TsOH, $CHCl_3$, 5 d, 25°	 (18) +  (12) +  (13) +  (5) +  (13)	498
	PBA, TsOH, $CHCl_3$, 48 h, 25°	 (13)	511
C_{28}			
	TFPAA, Na_2HPO_4, $CHCl_3$, 1.5 h, 30–40°	 I (65) +  II (14)	509, 510
	PBA, TsOH, $CHCl_3$, 7 d, 25°	I (10) + II (10) +  III (7)	512

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

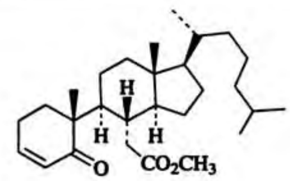
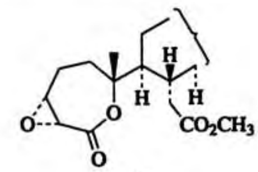
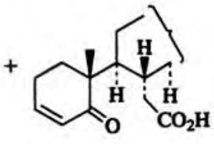
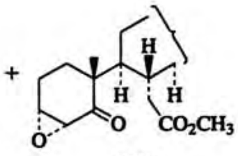
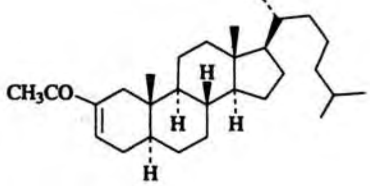
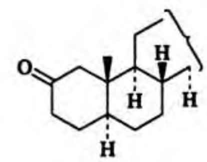
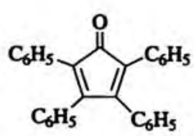
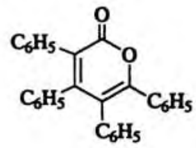
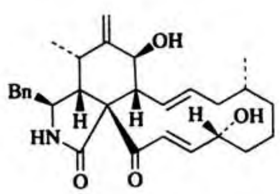
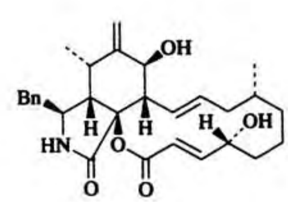
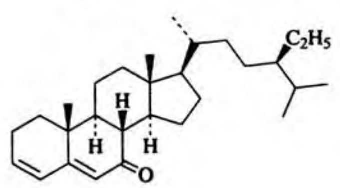
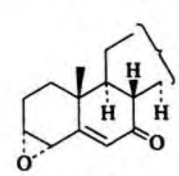
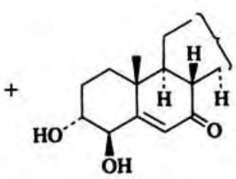
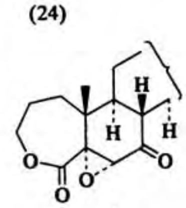
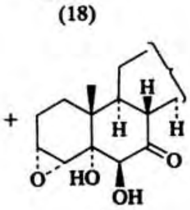
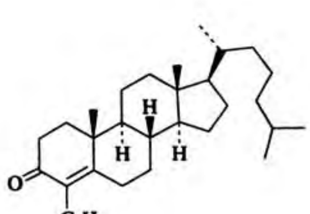
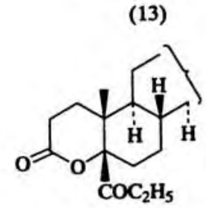
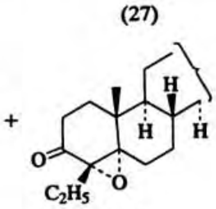
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PBA, TsOH, $CHCl_3$, 96 h, 25°	 (8) +  (6) +  (20) (5)*	169
C_{29}			
	MCPBA, H_2SO_4, $CHCl_3$, 25°	 (36) (40)*	488
	$[(CH_3)_3SiO]_2$, CH_2Cl_2, 8 h, 30°	 (76)	47
	PAA, TsOH, AcOH, 110 h, 23°	 (trace)	1089
	PBA, TsOH, $CHCl_3$, 48 h, 25°	 (24) +  (18) +  (13) +  (27)	504
	PBA, TsOH, $CHCl_3$, 7 d, 25°	 (15) +  (15)	512

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

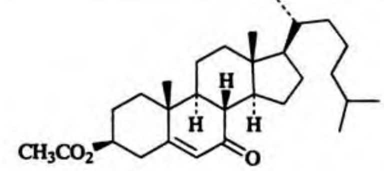
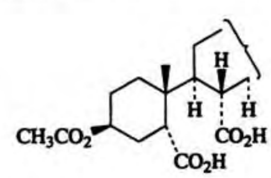
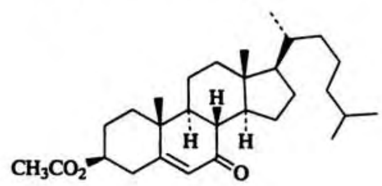
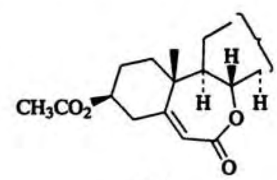
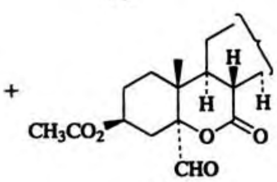
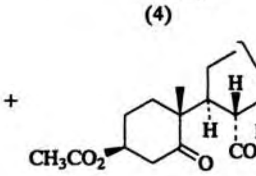
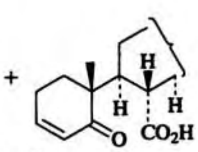
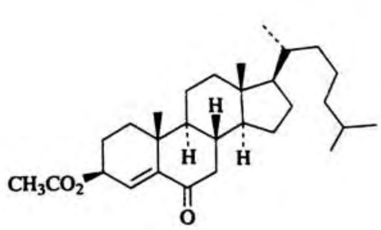
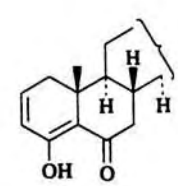
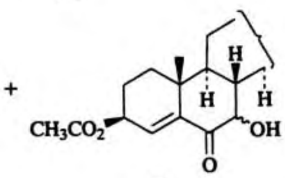
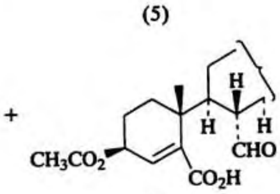
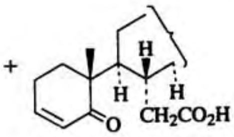
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	TFPAA, Na_2HPO_4, CH_2Cl_2, 75 min, 25°	 (—)	506
	PBA, TsOH, $CHCl_3$, 48 h, 25°	 (5) +  (4) +  +  (9–10)	511
	MCPBA (1 eq), TsOH, $CHCl_3$, 45 h, 25°	 I (6) +  II (5) +  III (19) +  IV (31) (31)*	501

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

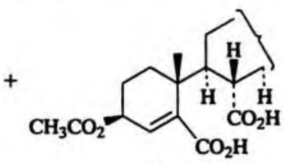
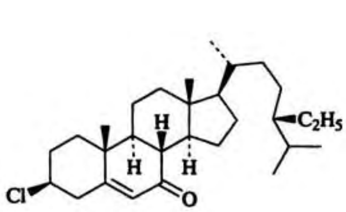
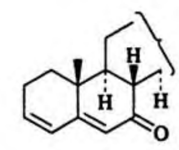
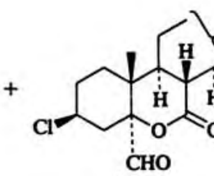
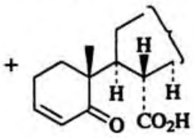
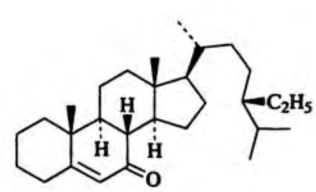
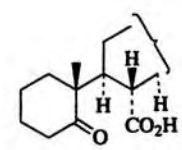
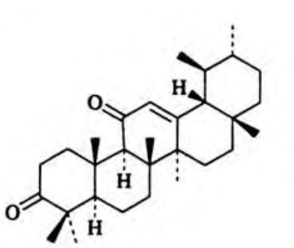
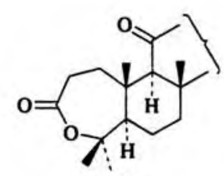
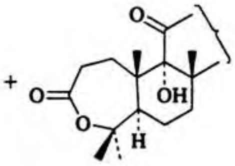
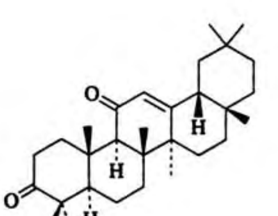
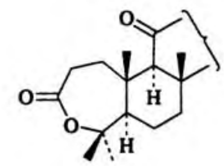
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA (2.5 eq), TsOH, $CHCl_3$, 45 h, 25°	III + IV +  V (13) (26) (14)	501
	PBA (1 eq), TsOH, $CHCl_3$, 48 h, 25°	 (22) +  (14) +  (22)	504
	PBA (2 eq), TsOH, $CHCl_3$, 48 h, 25°	 (56)	504
C_{30}			
	PBA (1 eq), $CHCl_3$, 45 h, 25°	 major +  minor (—)	502
	PBA, $CHCl_3$, 48 h, 5°	 (—)	502

TABLE V. REACTIONS OF α,β-UNSATURATED KETONES (*Continued*)

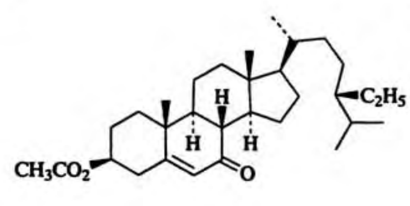
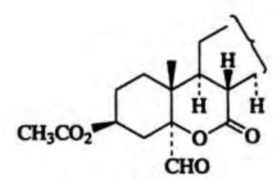
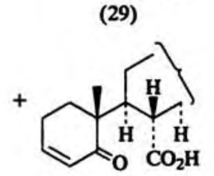
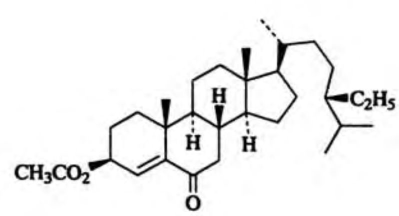
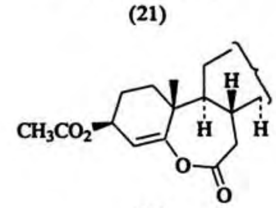
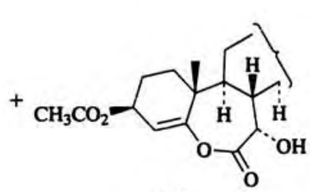
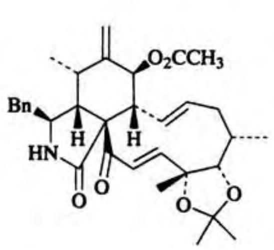
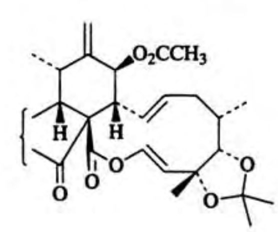
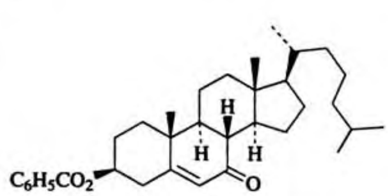
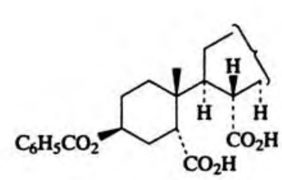
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{31}			
	PBA (2 eq), TsOH, $CHCl_3$, 48 h, 25°	 (29) (20)* +  (21)	504
	PBA (1 eq), TsOH, $CHCl_3$, 5 d, 25°	 (39) +  (19)	500
C_{33}			
	30% H_2O_2, AcOH, $CHCl_3$, 48 h, 50°	 (12) (60)*	495
C_{34}			
	TFPAA, Na_2HPO_4, CH_2Cl_2, 75 min, 25°	 (—)	506

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS

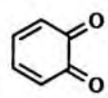
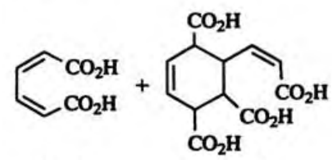
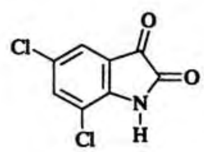
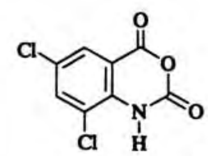
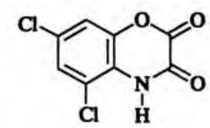
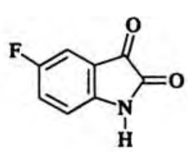
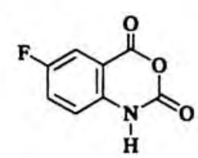
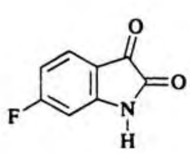
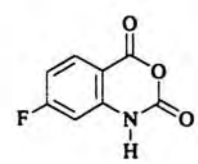
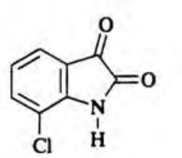
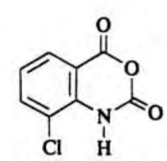
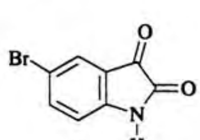
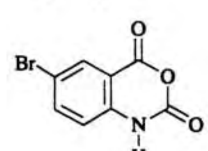
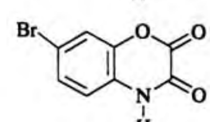
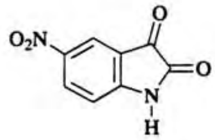
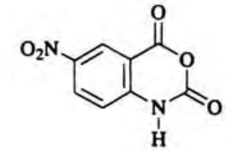
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4				
$CH_3COCOCH_3$	99% MCPBA, CH_2Cl_2, 25°	$(CH_3CO)_2O$	(100)	218
C_6				
	H_2O_2 (anh), ether–$CHCl_3$, 15 h, −5°	 (5–15) (20–25)		530, 536
C_8				
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(90)	541
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°		(95)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(83)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(84)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(85)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(83)	541
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°		(95)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(80)	541

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS (*Continued*)

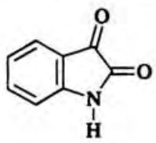
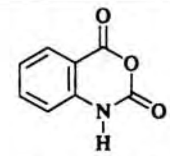
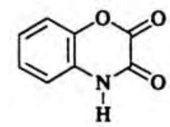
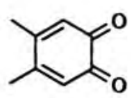
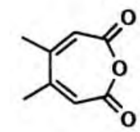
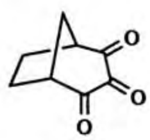
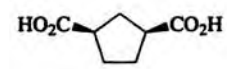
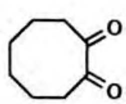
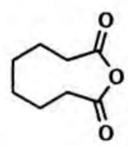
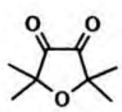
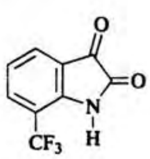
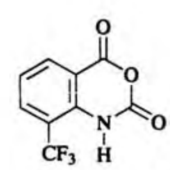
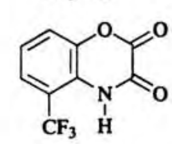
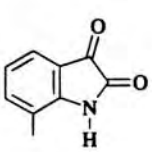
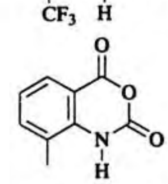
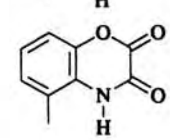
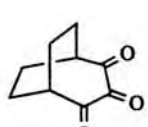
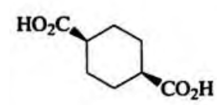
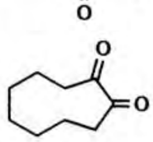
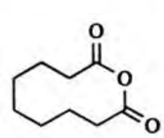
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(79)	541
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°		(95)	541
	MPPA, ether, 4 d, 0°		(—)	527
	H_2O_2, AcOH		(67)	535
	99% MCPBA, CH_2Cl_2, 25°		(100)	218
	H_2O_2, NaOH	$HO_2CC(CH_3)_2OC(CH_3)_2CO_2H$	(—)	534
C_9				
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(81)	541
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°		(82)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum		(75)	541
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°		(89)	541
	H_2O_2, AcOH		(53)	535
	99% MCPBA, CH_2Cl_2, 25°		(100)	218

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS (*Continued*)

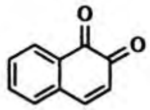
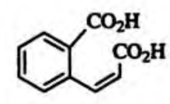
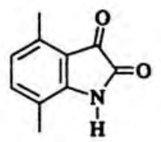
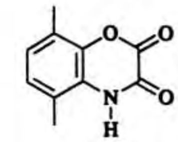
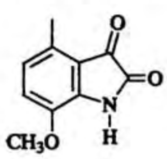
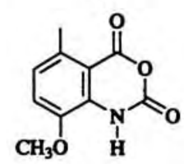
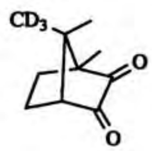
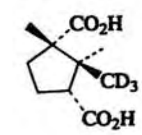
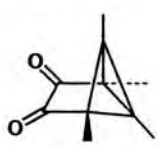
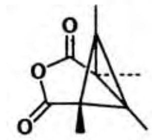
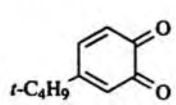
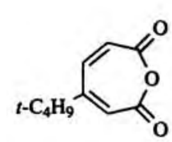
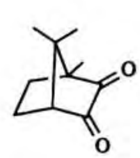
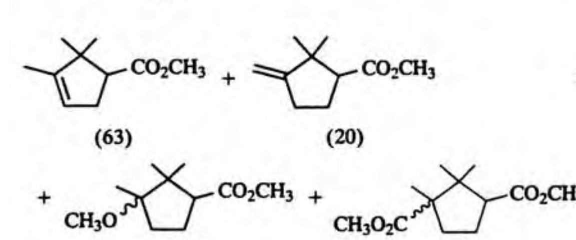
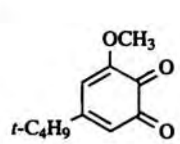
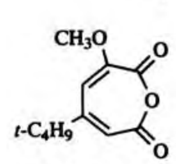
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
	H_2O_2, 75% HCO_2H, NaOH, 1 h, 23°	 (54)	31
	$K_2S_2O_8$, 85–95% H_2SO_4, a few min, 0–10°	 (90)	541
	30% H_2O_2, H_2SO_4, AcOH, 2 h, 25–35° to 60–70° maximum	 (70)	541
	30% H_2O_2, NaOH, 42 h, 25°	 (94)	533
	MCPBA, $CHCl_3$, 25°	 (—)	490
	85% MCPBA, CH_2Cl_2, 5–10 min, 0°	 (64)	526
	CAN, CH_3OH, 30 min, 25°	 (63) + (20) + (12) + (4)	691
C_{11}			
	MCPBA, CH_2Cl_2, 5–10 min, 0°	 (52)	526
p-$FC_6H_4COP(O)(OC_2H_5)_2$	PBA, C_6H_6 or $CH_3CO_2C_2H_5$, 3–5 d, 32°, or 13–16 d, 25°	p-$FC_6H_4CO_2P(O)(OC_2H_5)_2$ (70–85) + p-$FC_6H_4CO_4CC_6H_5$ (2–4) + $C_2H_5O_2CC_6H_5$ (2–6) + p-$FC_6H_4CO_3CC_6H_5$ (10–20) + $(C_2H_5O)_2P(O)OH$ (—)	544
m-$ClC_6H_4COP(O)(OC_2H_5)_2$	PBA, C_6H_6 or $CH_3CO_2C_2H_5$, 3–5 d, 32°, or 13–16 d, 25°	m-$ClC_6H_4CO_2P(O)(OC_2H_5)_2$ (70–85) + m-$ClC_6H_4CO_4CC_6H_5$ (2–4) + $C_2H_5O_2CC_6H_5$ (2–6) + m-$ClC_6H_4CO_3CC_6H_5$ (10–20) + $(C_2H_5O)_2P(O)OH$ (—)	544

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS (*Continued*)

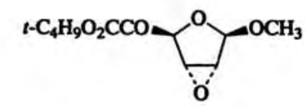
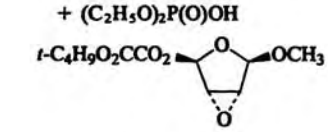
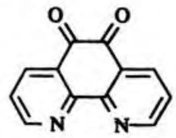
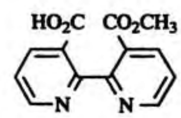
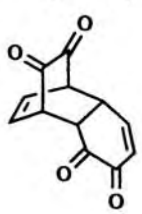
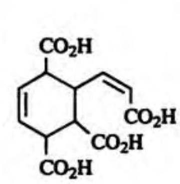
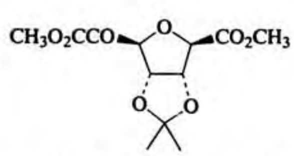
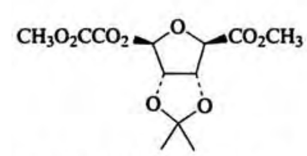
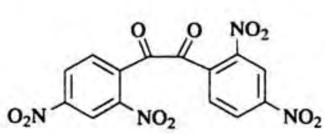
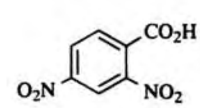
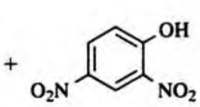
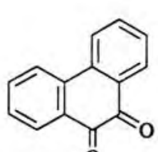
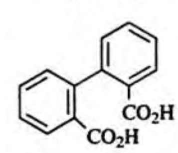
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
$C_6H_5COP(O)(OC_2H_5)_2$	PBA, benzene or $CH_3CO_2C_2H_5$, 3–5 d, 32°, or 13–16 d, 25°	$C_6H_5CO_2P(O)(OC_2H_5)_2$ + $C_6H_5CO_4CC_6H_5$ + $C_2H_5O_2CC_6H_5$ + $C_6H_5CO_3CC_6H_5$ + $(C_2H_5O)_2P(O)OH$	(70–85) (2–4) (2–6) (10–20) (—)	544
	MCPBA, CH_2Cl_2		(—)	542
C_{12}				
	MCPBA, HCl, CH_3OH, 2 h, 25°		(70)	539
	H_2O_2(anh), ether–$CHCl_3$, 7 d, −5°		(78)	530
	MCPBA, $CHCl_3$		(>77)	542, 543
p-$CH_3OC_6H_4COP(O)(OC_2H_5)_2$	PBA, $CH_3CO_2C_2H_5$, 13–16 d, 25°	p-$CH_3OC_6H_4CO_2P(O)(OC_2H_5)_2$ + p-$CH_3OC_6H_4CO_4CC_6H_5$ + $C_2H_5O_2CC_6H_5$ + p-$CH_3OC_6H_4CO_3CC_6H_5$ + $(C_2H_5O)_2P(O)OH$	(70–85) (2–4) (2–6) (10–20) (—)	544
C_{14}				
	H_2O_2, CH_3OH, +64° to −53°	 (30–60) +  (16–66)		540
	H_2O_2, HCO_2H–THF–H_2O, 1 h, 23°		(—)	31
$C_6H_5COCOC_6H_5$	t-BuO_2H, KOH, 80°	$C_6H_5CO_2H$	(16) (80)*	532, 538

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS (*Continued*)

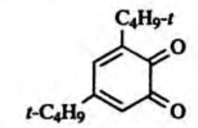
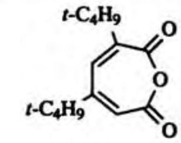
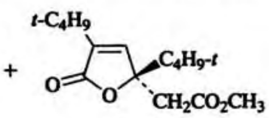
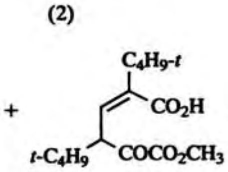
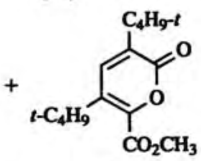
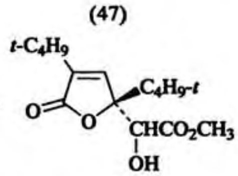
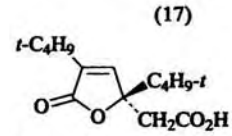
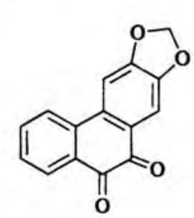
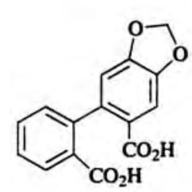
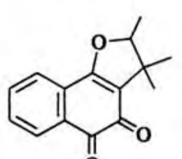
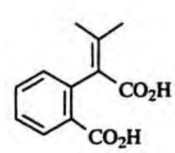
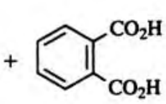
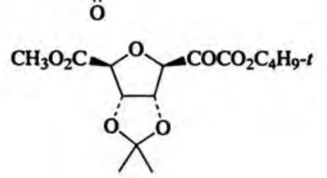
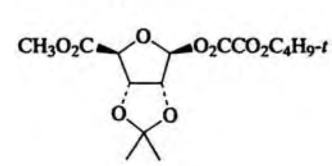
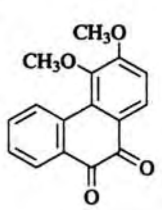
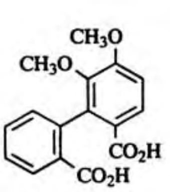
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, CH_3OH–H_2O, Na_2HPO_4, KH_2PO_4, 7 d, 25°	 I (2) +  II (24) +  (47) +  (8) +  (17)	525
	H_2O_2, NaOH, 75% HCO_2H, 1 h, 23°	 (31)	31
	H_2O_2, NaOH, CH_3OH, 5 d, 23°	II (10)	31
	MPPA, ether, 2 h, 0°	I (76)	523, 524, 525
C_{15}			
	35% H_2O_2, NaOH, CH_3OH–THF, >30 min, reflux	 (100)	531
	3% H_2O_2, NaOH	 +  (—)	674
	MCPBA, CH_2Cl_2	 (>32)	542, 543
C_{16}			
	35% H_2O_2, NaOH, CH_3OH, THF, 30 min, reflux	 (91)	531

TABLE VI. REACTIONS OF 1,2-DICARBONYL COMPOUNDS (*Continued*)

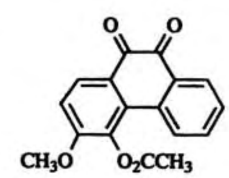
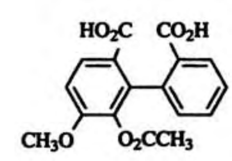
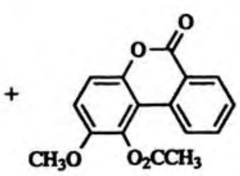
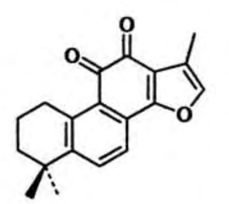
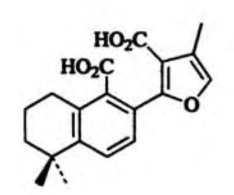
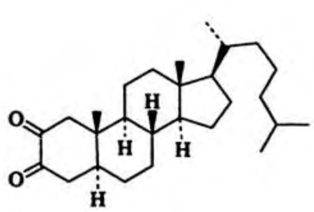
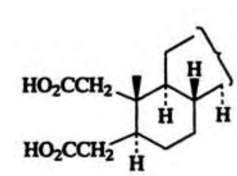
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}			
	PAA, AcOH, 3.5 h, 80–90°	 (74) +  (13)	537
C_{19}			
	MCPBA, CH_2Cl_2	 (2)	522
C_{29}			
	30% H_2O_2, SeO_2, *t*-BuOH, 15 h, reflux	 (8)	529

TABLE VII. REACTIONS OF ALDEHYDES

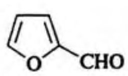
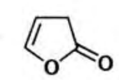
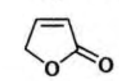
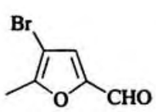
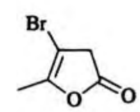
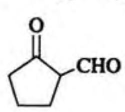
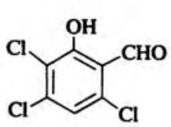
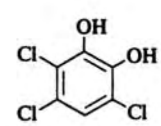
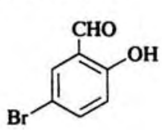
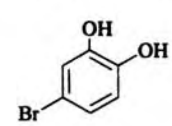
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_5				
	30% H_2O_2, HCO_2H, CH_2Cl_2, Na_2SO_4, 14 h, 25°		(21–26)	616
	1. 30% H_2O_2, HCO_2H, CH_2Cl_2, Na_2SO_4, K_2CO_3, 14 h, 25° 2. $(C_2H_5)_3N$, $C_6H_5CH_3$, 1 h, 25°		(50–54)	616
C_6				
	30% H_2O_2, HCO_2H, CH_2Cl_2, Na_2SO_4, 24 h, 25°		(69)	617
	30% H_2O_2, 0–90°	$HO_2C(CH_2)_4CO_2H$	(90)	203, 624
C_7				
	6% H_2O_2, NaOH, 12 h, 40–60°		(—)	545
p-ClC_6H_4CHO	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, reflux	p-$ClC_6H_4CO_2CH_3$	(87)	579
	3% H_2O_2, NaOH, 15 min, 25°		(75)	546

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

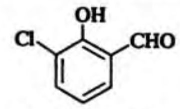
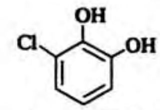
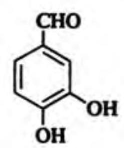
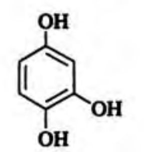
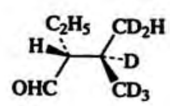
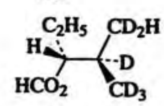
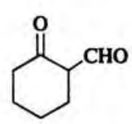
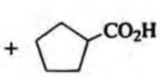
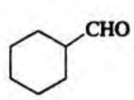
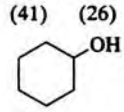
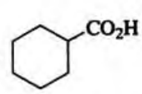
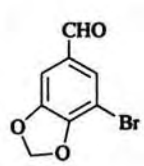
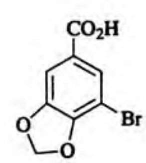
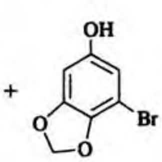
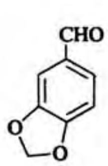
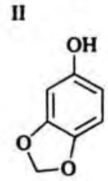
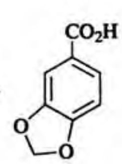
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	6% H_2O_2, NaOH, 12 h, 40–60°		(67)	545
p-$O_2NC_6H_4CHO$	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, reflux	p-$O_2NC_6H_4CO_2CH_3$	(80)	579
C_6H_5CHO	$KHSO_5$, H_2O, $CHCl_3$, H_2SO_4, 2 d, 25°	$C_6H_5CO_2H$ I	(49) (30)*	574, 589
	3% H_2O_2, NaOH, 1 h, heat	C_6H_5OH II	(0.5)	546
	MCPBA, CH_2Cl_2, argon, 25°	I + II (42) (32)		614
o-HOC_6H_4CHO	3% H_2O_2, NaOH, 45 min, 15°	o-HOC_6H_4OH	(96)	96, 546, 547
	$KHSO_5$, H_2O, $CHCl_3$, H_2SO_4, 8 h, 25°	"	(12) (83)*	574
p-HOC_6H_4CHO	3% H_2O_2, NaOH, 30 min, 20°	p-HOC_6H_4OH	(97)	96, 546, 548
	3% H_2O_2, NaOH, 1.5 h, 0°		(64)	96
	MCPBA		(—)	620
	H_2O_2, Cold	$HO_2C(CH_2)_5CO_2H$ I	(—)	624
	30% H_2O_2, 20 min, 25°	I +  II (35) (44)		202, 203
	1. 30% H_2O_2, t-BuOH, 50–55° 2. 12 h, 25°	I + II (41) (26)		78
	TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 25°	 +  (74) (19)		589, 619
C_8				
	35% H_2O_2, 85% HCO_2H, 4 h, 0°	 +  I II	(79)	602, 603
	MCPBA, $CHCl_3$, 90 min, heat	II	(93)	586
	20% PAA, AcOH, 24 h, 25°	 +  I II (68) (3)		605

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

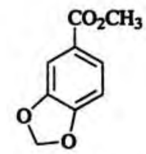
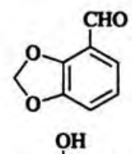
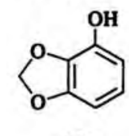
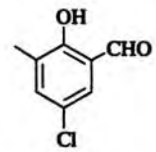
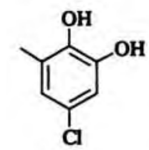
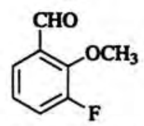
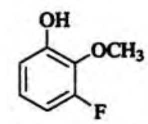
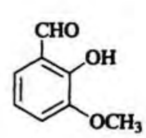
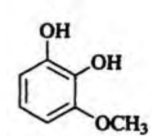
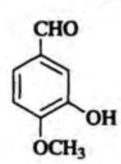
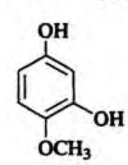
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, KF, CH_2Cl_2	I (95)	575
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 45 h, 25°	I (88)	578
	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, 25°	 (8)	579
	1. MCPBA 2. KOH	 (65)	587
	6% H_2O_2, NaOH, 12 h, 40–60°	 (72)	545
	MCPBA, CH_2Cl_2, 12 h, heat	 (73)	588
$C_6H_5CH_2CHO$	PAA, TFAA, 2 h, 25°	$C_6H_5CH_2O_2CH$ (81) + $C_6H_5CH_2CO_2H$ (11)	589
$p\text{-}CH_3C_6H_4CHO$	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, reflux	$p\text{-}CH_3C_6H_4OH$ (28) + $p\text{-}CH_3C_6H_4CO_2CH_3$ (51)	579, 1090
$o\text{-}CH_3C_6H_4CHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 27 h, 25°	$o\text{-}CH_3C_6H_4OH$ (94)	578
$p\text{-}CH_3OC_6H_4CHO$	3% H_2O_2, NaOH, 1 h, heat	$p\text{-}CH_3OC_6H_4OH$ I (0.8)	546
	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, reflux	I (90)	579
	MCPBA, CH_2Cl_2, 5 h, reflux	$p\text{-}CH_3OC_6H_4O_2CH$ (92)	584, 589
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 30 h, 25°	I (93)	578
$m\text{-}CH_3OC_6H_4CHO$	MCPBA, CH_2Cl_2, 29 h, reflux	$m\text{-}CH_3OC_6H_4O_2CH$ (31)	584
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 123 h, 25°	$m\text{-}CH_3OC_6H_4OH$ (14)	578
	31% H_2O_2, H_2SO_4, CH_3OH, 68 h, reflux	$m\text{-}CH_3OC_6H_4CO_2CH_3$ (68)	579
$o\text{-}CH_3OC_6H_4CHO$	MCPBA, CH_2Cl_2, 18.5 h, reflux	$o\text{-}CH_3OC_6H_4O_2CH$ (>60)	584
	TFPAA, Na_2HPO_4, CH_2Cl_2, 1 h	$o\text{-}CH_3OC_6H_4OH$ (81)	589
	31% H_2O_2, H_2SO_4, CH_3OH, 24 h, reflux	" (94)	579
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 12 h, 25°	" (93)	578
	6% H_2O_2, NaOH, 1 h, 40–50°	 (68–80)	549
	PAA, 12 h, 40°	 (74)	606
	MCPBA, KF, CH_2Cl_2	" (79)	575

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

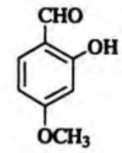
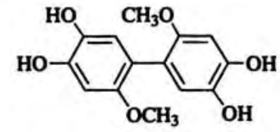
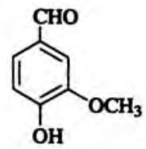
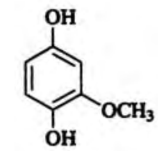
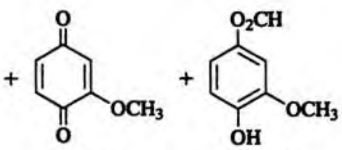
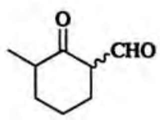
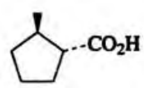
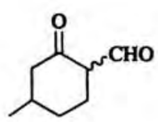
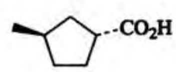
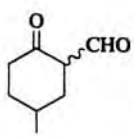
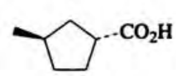
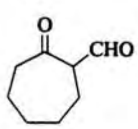
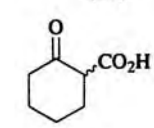
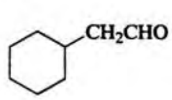
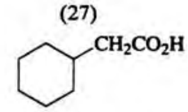
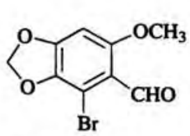
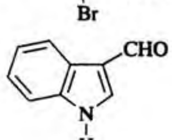
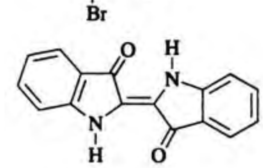
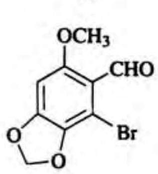
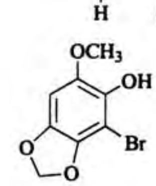
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	6% H_2O_2, NaOH, 1–2 h, 50°	 (58–60)	550
	3% H_2O_2, NaOH, 30 min, 20°	 I (97)	96, 546, 551
	MCPBA, KF, CH_2Cl_2	I (77)	575
	PAA, H_2O, (pH = 3), 1 h, 60°	I (22) +  (13) (11)	572
	30% H_2O_2, 20 min, 25–30°	 (52) + $HO_2CCH(CH_3)(CH_2)_4CO_2H$ (21)	202, 203
	30% H_2O_2, 20 min, 25–30°	 (59) + $HO_2CCH_2CH(CH_3)(CH_2)_3CO_2H$ (36)	203
	30% H_2O_2, 20 min, 25–30°	 (30) + $CH_3CH(CH_2CH_2CO_2H)_2$ (57)	203
	30% H_2O_2, NaOH, 1 h, 20–25°	 (27) + $HO_2C(CH_2)_6CO_2H$ (33)	202, 204
	MCPBA, MCBA, $CHCl_3$, 27°	 (major) (—)	619
C_9			
	35% H_2O_2, HCO_2H	 (71)	603
	3% H_2O_2, NaOH, 10 min, 25°	 (70)	546
	35% H_2O_2, 85% HCO_2H, 5 h, 0–5°	 (73)	602

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

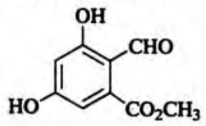
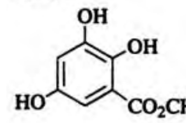
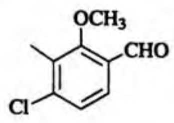
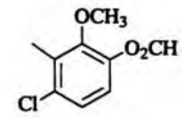
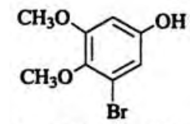
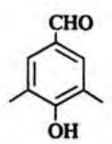
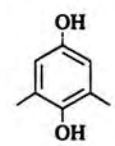
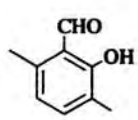
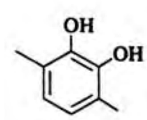
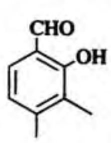
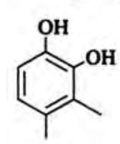
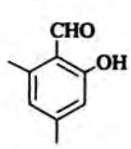
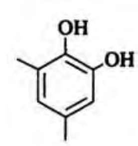
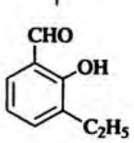
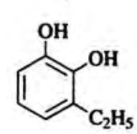
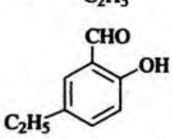
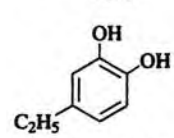
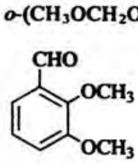
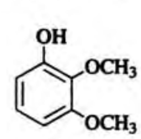
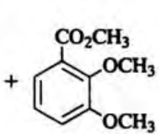
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6H_5COCH_2CHO$	30% H_2O_2, KOH, 25–30°	$C_6H_5CO_2H$ (41)	203
	H_2O_2, NaOH, 25°	 (70)	552
	MCPBA, CH_2Cl_2, 48 h, reflux	 (82)	584
	MCPBA, $CHCl_3$, 45 min, reflux	 (82)	585
$C_6H_5CH(CH_3)CHO$	TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 25°	$C_6H_5CH(CH_3)OH$ (84) + $C_6H_5CH(CH_3)CO_2H$ (2)	589
$C_6H_5(CH_2)_2CHO$	PAA, TFAA, 2 h, 25°	$C_6H_5(CH_2)_2OH$ (11) + $C_6H_5(CH_2)_2CO_2H$ (85)	589
o-$C_2H_5OC_6H_4CHO$	30% H_2O_2, (o-$O_2NC_6H_4Se)_2$, CH_2Cl_2, 20 h, 25°	o-$C_2H_5OC_6H_4OH$ (93)	578
	3% H_2O_2, KOH, 15–40 min, 25°	 (91)	548
	6% H_2O_2, NaOH, 12 h, 40–60°	 (71)	545
	6% H_2O_2, NaOH, 12 h, 40–60°	 (54)	545
	6% H_2O_2, NaOH, 12 h, 40–60°	 (77)	545
	6% H_2O_2, NaOH, 12 h, 40–60°	 (67)	545
	6% H_2O_2, NaOH, 12 h, 40–60°	 (86)	545
o-$(CH_3OCH_2O)C_6H_4CHO$	30% H_2O_2, (o-$O_2NC_6H_4Se)_2$, CH_2Cl_2, 9 h, 25°	o-$(CH_3OCH_2O)C_6H_4OH$ (79)	578
	31% H_2O_2, H_2SO_4, CH_3OH, 63 h, 25°	 +  I (30) II (14)	579

TABLE VII. Reactions of Aldehydes (*Continued*)

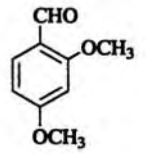
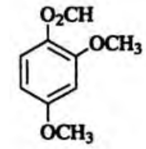
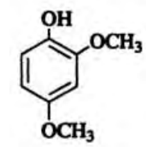
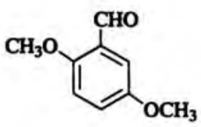
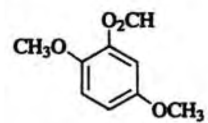
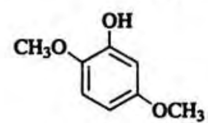
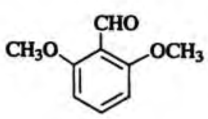
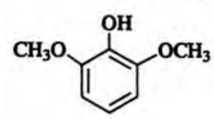
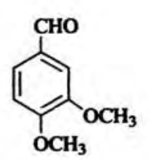
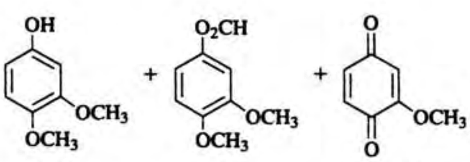
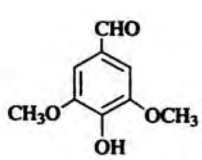
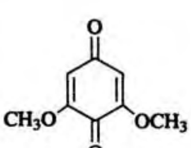
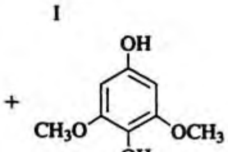
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 52 h, 25°	I	(95)	578
	MCPBA, CH_2Cl_2, 16 h, reflux		(80)	584
	31% H_2O_2, H_2SO_4, CH_3OH, 14 h, 25°	 I	(90)	579
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 17 h, 25°	I	(95)	578
	MCPBA, CH_2Cl_2, 5 h, 25°		(90)	580
	1. 30% H_2O_2, $[2,4\text{-}(NO_2)_2C_6H_3Se]_2$, CH_2Cl_2, 25° 2. KOH, CH_3OH, 1 h		(80)	596
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 9 h, 25°		(90)	578
	PAA, H_2O, pH 3, 1 h, 60°	 I (12) + II (9) + III (6)	+(7)*	572
	MCPBA, KF, CH_2Cl_2	I	(90)	575, 584
	20% PAA, AcOH, 24 h, 25°	I	(63) +(21)*	605
	31% H_2O_2, H_2SO_4, CH_3OH, 5 h, 25°	I	(60)	579
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 27 h, 25°	I	(87)	578
	PAA, $HClO_4$, AcOH, >15 min, 25°	 I	(40)	573
	PAA, H_2O, pH 3, 1 h, 60°	I +  (80) (4)	+(5)*	572
$n\text{-}C_4H_9CH(C_2H_5)CHO$	PAA, AcOH, 20 h, 20–25°	$n\text{-}C_4H_9CH(C_2H_5)O_2CH$ (25–30) + $n\text{-}C_4H_9CH(C_2H_5)CO_2H$ (40)		623

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

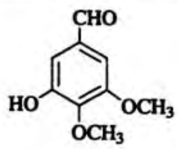
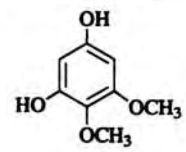
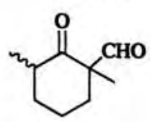
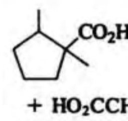
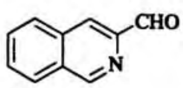
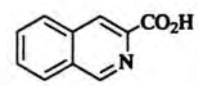
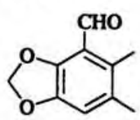
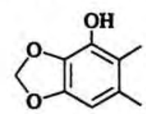
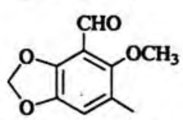
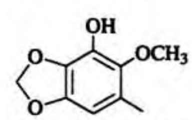
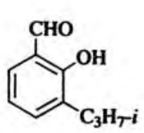
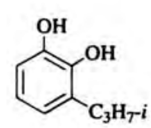
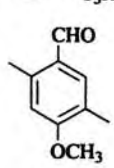
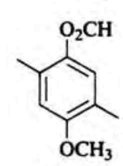
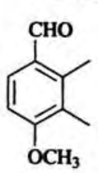
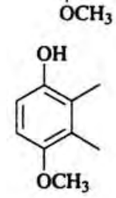
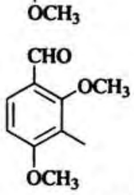
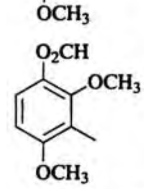
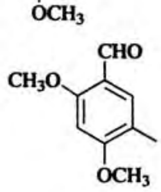
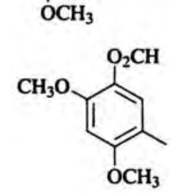
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCO_3H, HCO_2H	 (—)	1091
	28% H_2O_2, H_2O, 12 h, 20°	 (51)	202, 204
		+ $HO_2CCH(CH_3)(CH_2)_3CH(CH_3)CO_2H$ (25)	
		+ $HO_2CCH(CH_3)(CH_2)_3CO_2H$ (6)	
C_{10}			
	30% H_2O_2, $(CH_3)_2CO$, 12 h, 25°	 (96)	618
	30% H_2O_2, 85% HCO_2H, 24 h, 0°	 (55)	604
	30% H_2O_2, 85% HCO_2H, 24 h, −5°	 (63)	604
2,4,6-$(CH_3)_3C_6H_2CHO$	30% H_2O_2, $[2,4\text{-}(NO_2)_2C_6H_3Se]_2$, CH_2Cl_2, 28 h, 25°	2,4,6-$(CH_3)_3C_6H_2OH$ (91)	578
2-(n-C_3H_7O)C_6H_4CHO	30% H_2O_2, (o-$O_2NC_6H_4Se)_2$, CH_2Cl_2, 34 h, 25°	2-(n-C_3H_7O)C_6H_4OH (96)	578
	6% H_2O_2, NaOH, 12 h, 40–60°	 (68)	545
	MCPBA, CH_2Cl_2, 21 h, reflux	 (92)	584
	30% H_2O_2, o-$O_2NC_6H_4SeO_2H$, CH_2Cl_2, 33 h, 25°	 (89)	578
	MCPBA, CH_2Cl_2, 24 h, reflux	 (96)	584, 590, 591
	MCPBA, CH_2Cl_2, 24 h, reflux	 (65)	584, 591

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

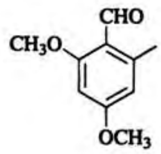
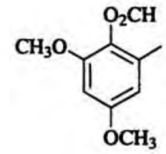
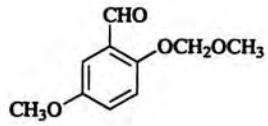
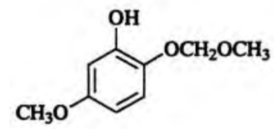
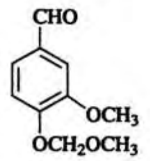
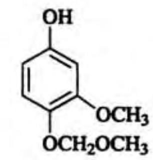
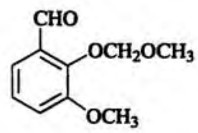
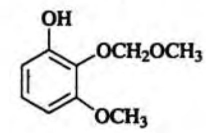
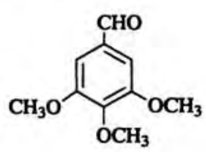
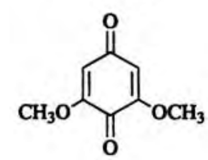
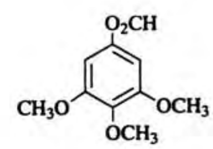
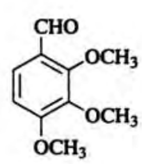
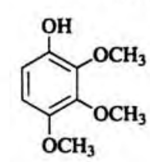
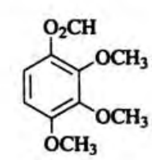
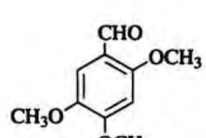
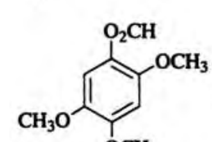
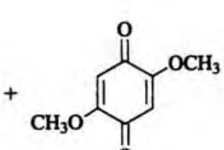
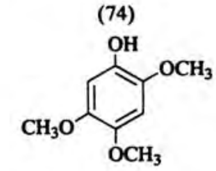
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, 50 h, reflux		(89)	584
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 16 h, 25°		(93)	578
	1. 30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 25° 2. KOH, CH_3OH, 1 h		(74)	578, 596
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 16 h, 25°		(73)	578
	PAA, $HClO_4$, AcOH, 25°		(50)	573
	35% PAA, $HClO_4$, Ac_2O, 1 h, 0–5°		(59)	607
	31% H_2O_2, H_2SO_4, CH_3OH, 1 h, 25°		(97)	579, 591
	40% PAA, H_2SO_4, CH_3OH–H_2O, 2 h, 20°	"	(95)	608
	35% PAA, $HClO_4$, Ac_2O, 2 h, 13°		(67)	607
	MCPBA, CH_2Cl_2, 24 h, reflux	"	(83)	584
	35% PAA, $HClO_4$, Ac_2O	 +  (74) (9)		607
	1. MCPBA, CH_2Cl_2, 48 h, heat 2. KOH, CH_3OH, 25°		(79)	584

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

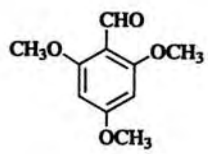
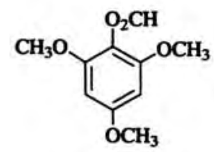
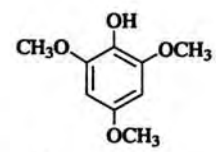
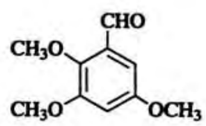
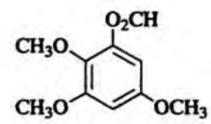
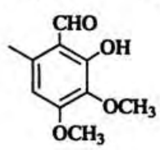
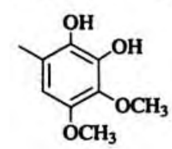
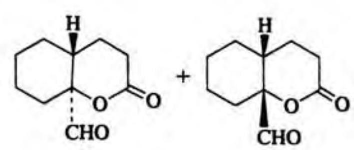
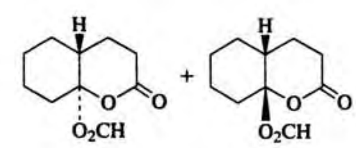
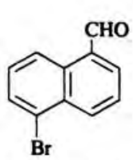
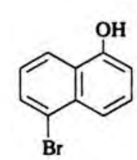
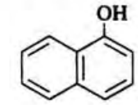
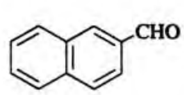
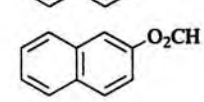
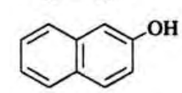
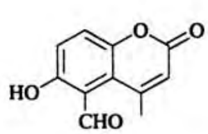
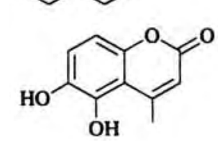
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	31% H_2O_2, H_2SO_4, CH_3OH, 4 h, 25°	"	(89)	579
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 24 h, 25°	"	(88)	578
	35% PAA, $HClO_4$, Ac_2O, 1 h		(70)	607
	MCPBA, CH_2Cl_2, 2 h, 0–25°		(64)	583
	31% H_2O_2, H_2SO_4, CH_3OH, 2 h, 25°	"	(89)	579
	MCPBA, CH_2Cl_2, 48 h, reflux		(79)	584
	6% H_2O_2, NaOH, 1 h, 10°		(67)	553
 I II I:II = 50:50	MCPBA (85%), CH_2Cl_2, 24 h, 12°	 I II I:II = 50:50	(85)	298
C_{11}				
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 58 h, 25°		(91)	578
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF (anh), 4–5 h		(92)	613, 614
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 21 h, 25°		(91)	578
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF (anhydrous), 4–5 h		(80)	613, 614
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 80 h, 25°		(67)	578
	6% H_2O_2, NaOH, 1 h, 0°		(—)	557

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

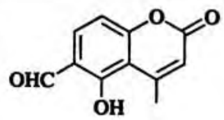
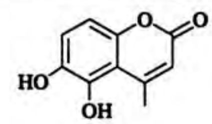
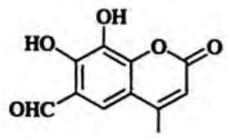
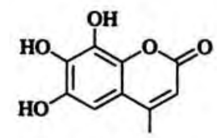
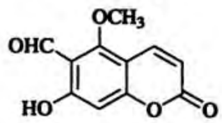
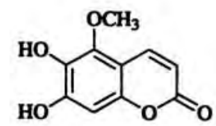
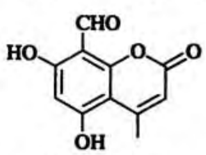
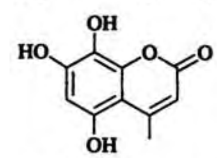
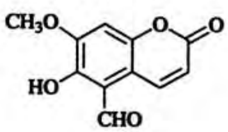
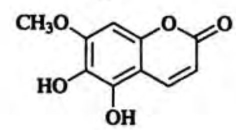
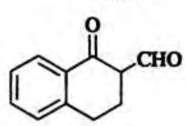
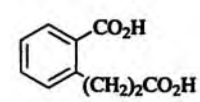
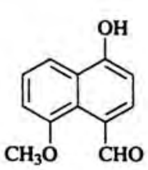
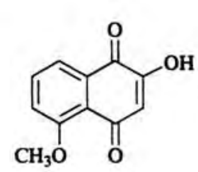
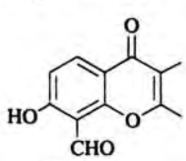
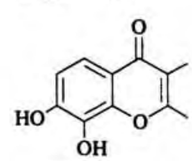
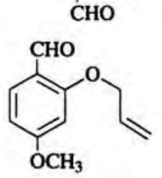
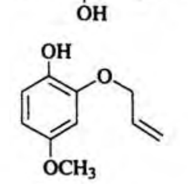
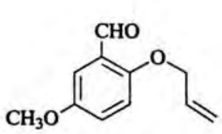
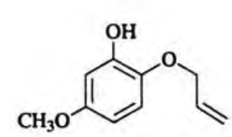
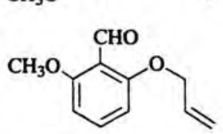
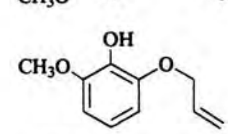
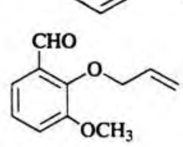
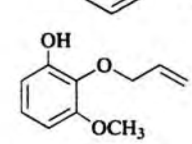
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	6% H_2O_2, NaOH, 1 h, 0°		(—)	557
	6% H_2O_2, NaOH, 1 h, 0°		(—)	557
	30% H_2O_2, NaOH, 12 h, 0°		(63)	569
	6% H_2O_2, NaOH, 1 h, 0°		(63)	558
	6% H_2O_2, NaOH, C_5H_5N, 1.25 h, 0–10°		(53)	562
	30% H_2O_2, Na_2CO_3-H_2O, 1 h, 20–25°		(80)	204
	30% H_2O_2, KOH, H_2O, 30 min, 25°	 + hydroxy isomer	(73)	571
	4.9% H_2O_2, NaOH, 1.5 h, 25°		(—)	566
	85% MCPBA, CH_2Cl_2, 24 h, 25°		(77)	610
	31% H_2O_2, $KHSO_4$, CH_3OH, 4 h, 25°	"	(83)	579
	85% MCPBA, CH_2Cl_2, 24 h, 25°		(100)	610
	85% MCPBA, CH_2Cl_2, 20 h, 25°		(100)	610
	85% MCPBA, CH_2Cl_2, 20 h, 25°		(69)	610

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

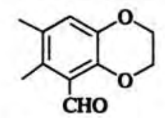
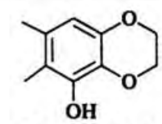
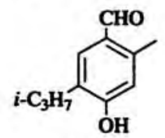
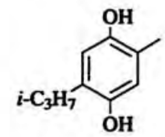
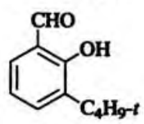
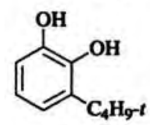
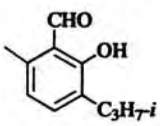
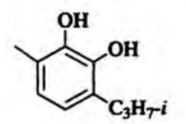
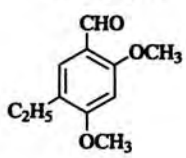
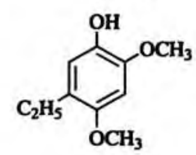
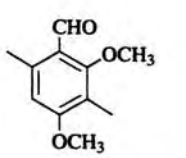
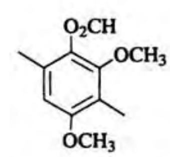
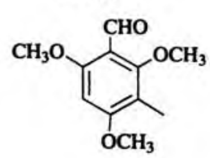
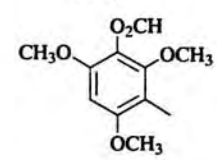
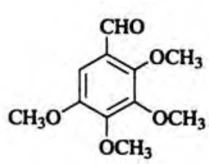
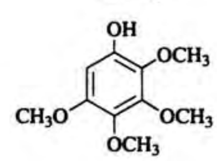
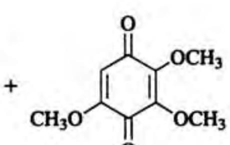
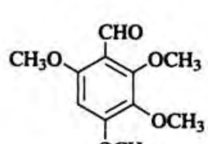
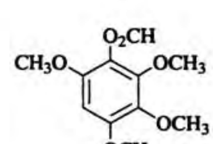
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, 85% HCO_2H, 24 h, −5°	 (54)	604
2,3,5,6-$(CH_3)_4C_6HCHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 16 h, 25°	2,3,5,6-$(CH_3)_4C_6HOH$ (88)	578
2,3,4,6-$(CH_3)_4C_6HCHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 18 h, 25°	2,3,4,6-$(CH_3)_4C_6HOH$ (98)	578
o-(i-$C_4H_9O)C_6H_4CHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 31 h, 25°	o-(i-$C_4H_9O)C_6H_4OH$ (81)	578
	3% H_2O_2, NaOH, immediate, 25°	 (64)	555
	6% H_2O_2, NaOH, 12 h, 40–60°	 (57)	545
	6% H_2O_2, NaOH, 12 h, 40–60°	 (82)	545
	30% H_2O_2, 85% HCO_2H, 38 h, 25°	 (19)	591
	MCPBA, CH_2Cl_2, 12 h, reflux	 (88)	584
	MCPBA, CH_2Cl_2, 2 h, 0–25°	 (64)	583
	35% PAA, $HClO_4$, Ac_2O, 3 h, −15 to 5°	 I (62) +  II (6)	607
	1. 80% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 45 h, 25° 2. KOH, CH_3OH, 1 h	I (94)	578, 596
	DNPBA, CH_2Cl_2, 1.5 h, 20°	 I (94)	600
	MCPBA, CH_2Cl_2, 96 h, reflux	I (82)	584

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

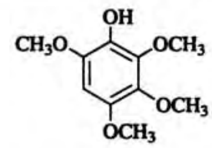
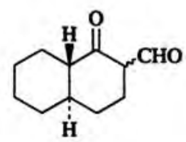
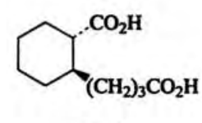
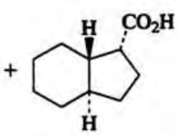
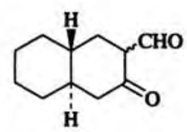
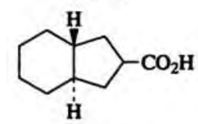
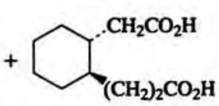
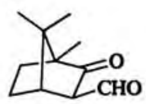
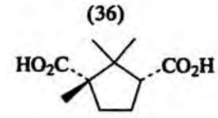
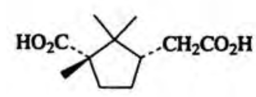
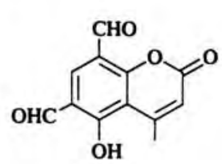
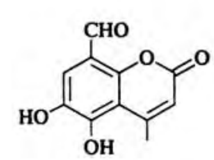
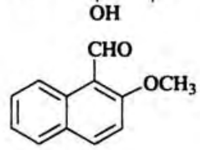
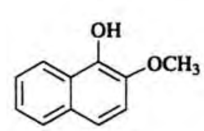
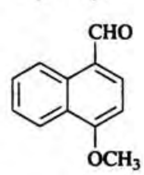
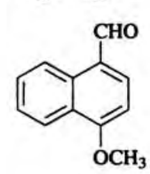
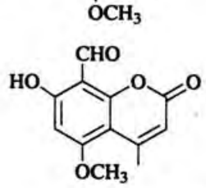
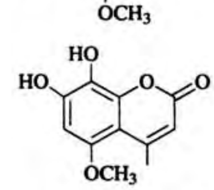
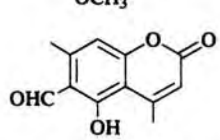
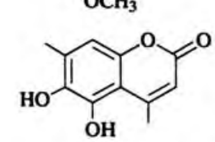
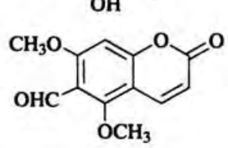
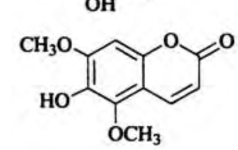
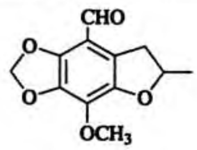
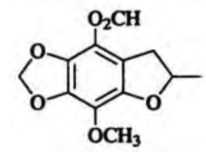
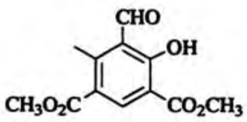
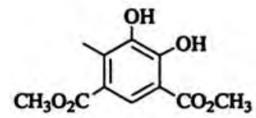
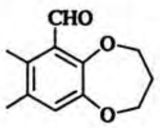
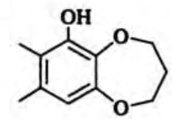
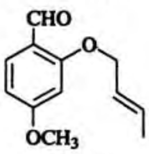
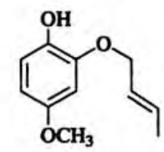
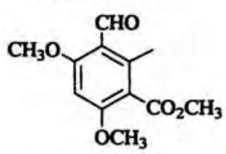
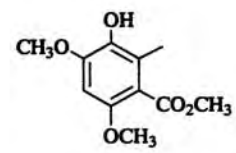
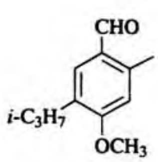
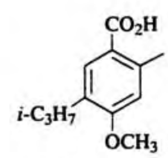
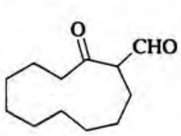
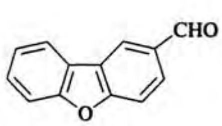
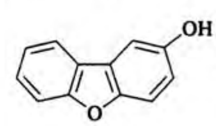
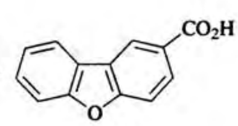
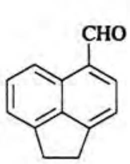
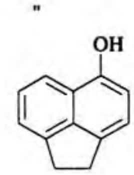
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 9 h, 25°		(93)	578, 596
	30% H_2O_2, 3 h, 25°	 (16) +  (60)		82
	6% H_2O_2, NaOH, 1 h, 0°	 (36) +  (24)		81
	1. 28% H_2O_2, KOH–H_2O, 40 min, 29° 2. 12 h, 20°		(62)	202
	28% H_2O_2, AcOH, 12 h, 20°		(33)	202
C_{12}				
	6% H_2O_2, NaOH, 1 h, 0°		(—)	557
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 25 h, 25°		(98)	578
	30% H_2O_2, $o\text{-}O_2NC_6H_4SeO_2H$, CH_2Cl_2, 27 h, 25°		(79)	578
	6% H_2O_2, NaOH, 2 h, 0°		(53)	558
	6% H_2O_2, NaOH, 1 h, 0°		(—)	558
	30% H_2O_2, 50% H_2SO_4, AcOH, 16 h, 0°		(74)	569

TABLE VII. Reactions of Aldehydes (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCO_3H, 16 h, −5°	 (50)	601
	28% H_2O_2, KOH, 3 h, 40°	 (75)	570
	50% H_2O_2, 85% HCO_2H, 24 h, −5°	 (62)	604
	31% H_2O_2, $KHSO_4$, CH_3OH, 4 h, 25°	 (97)	579
	MCPBA, CH_2Cl_2, reflux	 (—)	592
	30% H_2O_2, K_2CO_3, 15 h, 25°	 (—)	555
$(CH_3)_5C_6CHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 60 h, 25°	$(CH_3)_5C_6OH$ (77)	578
	28% H_2O_2, AcOH	$HO_2C(CH_2)_{11}CO_2H$ + $HO_2C(CH_2)_{10}CO_2H$ I (56) II (4)	202
	28% H_2O_2, KOH, 12 h, 20°	I + II (25) (27)	202
C_{13}			
	MCPBA, CH_2Cl_2, argon, 20 h, 25°	 I (85) +  II (2)	614
	30% H_2O_2, HCO_2H, 20 h, 25°	I + II (81) (1)	614
$p\text{-}C_6H_5C_6H_4CHO$	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 60 h, 25°	$p\text{-}C_6H_5C_6H_4OH$ (77)	578
	MCPBA, CH_2Cl_2, 25°	" (80)	614
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 25 h, 25°	 (92)	578

738

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TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

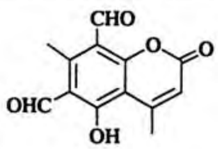
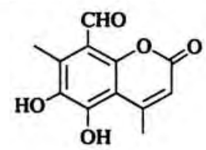
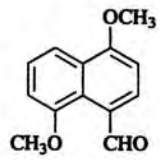
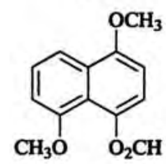
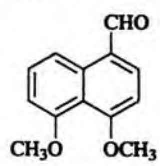
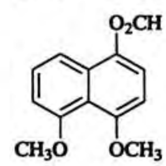
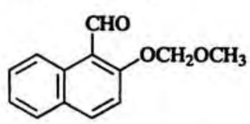
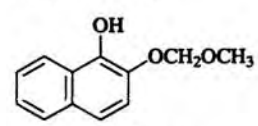
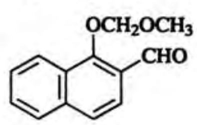
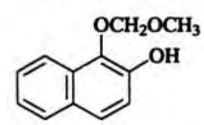
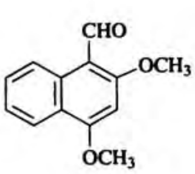
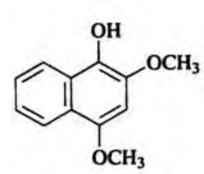
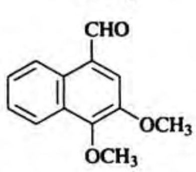
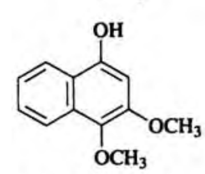
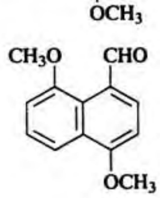
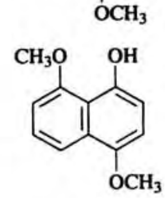
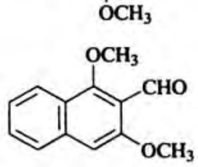
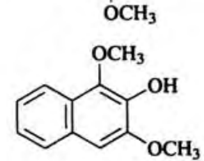
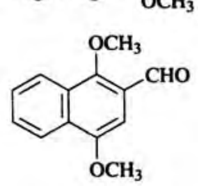
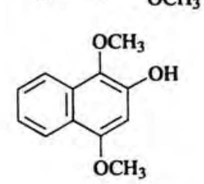
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	6% H_2O_2, NaOH, 1 h, 0°		(—)	557
	MCPBA, CH_2Cl_2, 2.3 h, 25°		(99)	571
	PNPBA, K_2CO_3, $CH_3CO_2C_2H_5$, 3 h, 25°		(79)	615
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 28 h, 25°		(89)	578
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 31 h, 25°		(97)	578
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 17 h, 25°		(54)	578
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 38 h, 25°		(73)	578, 596
	1. 30% H_2O_2, $o\text{-}O_2NC_6H_4SeO_2H$, CH_2Cl_2, 26 h, 25° 2. 10% HCl, acetone, 30 min, heat		(83)	577, 578
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 97 h, 25°		(82)	578
	1. 30% H_2O_2, $o\text{-}O_2NC_6H_4SeO_2H$, CH_2Cl_2, 30 h, 25° 2. 10% HCl, acetone, 30 min, heat		(93)	577, 578

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

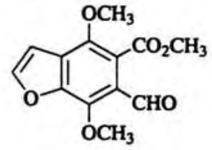
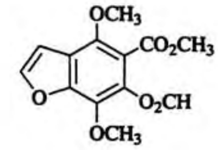
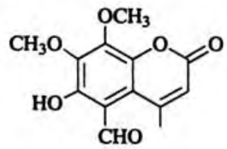
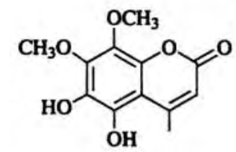
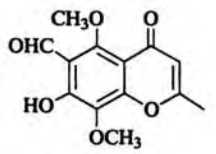
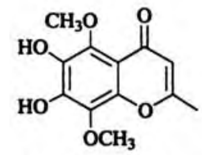
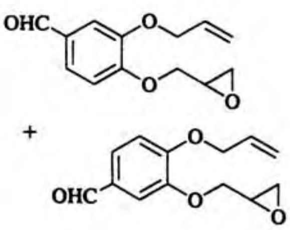
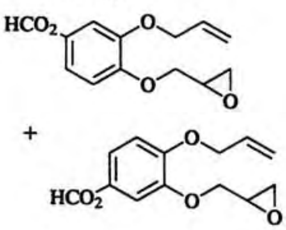
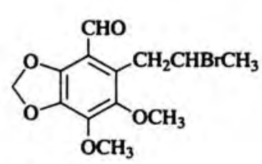
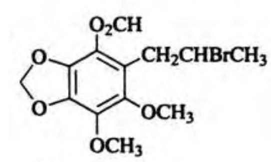
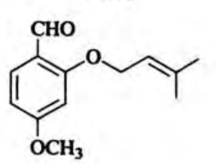
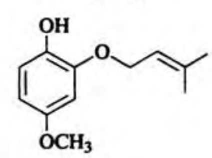
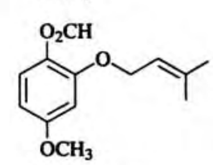
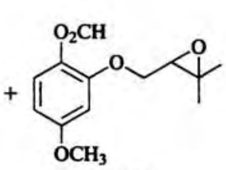
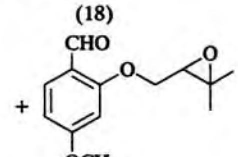
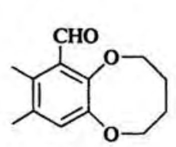
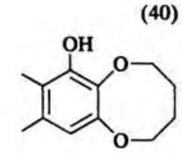
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	85% MCPBA, i-C_3H_7OH, 16 h, 25°	 (63)	581, 582
	6% H_2O_2, NaOH, 1 h, 0°	 (35	557
	30% H_2O_2, NaOH, 2.5 h, 25°	 (70)	567
	85% MCPBA, CH_2Cl_2, 20 h, 25°	 (100)	610
	HCO_3H, 16 h, −5°	 (30)	601
	31% H_2O_2, $KHSO_4$, CH_3OH, 4 h, 25°	 (80)	579
	MCPBA	 (18) +  (30) +  (40)	579
	50% H_2O_2, 85% HCO_2H, 24 h, −5°	 (52)	604

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

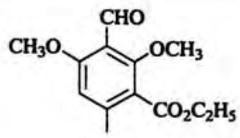
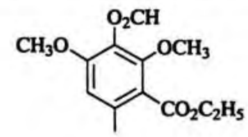
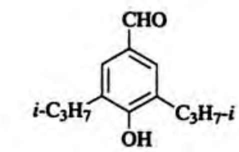
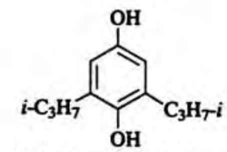
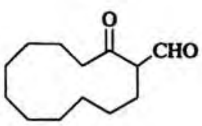
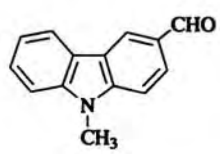
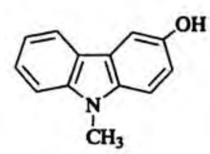
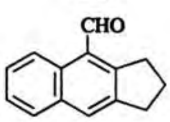
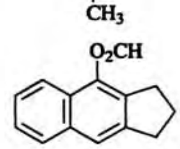
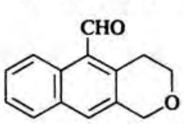
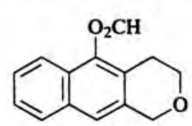
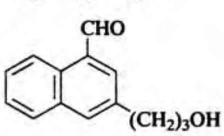
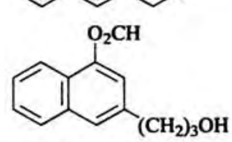
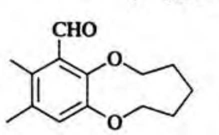
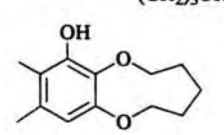
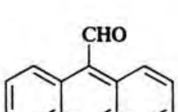
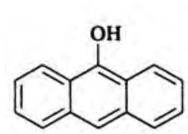
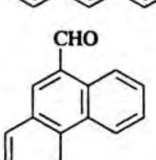
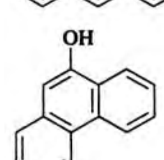
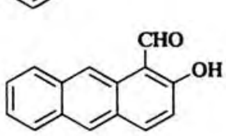
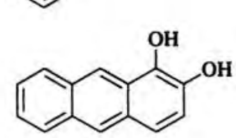
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, CH_2Cl_2, 90 h, reflux	 (80)	584
	3% H_2O_2, KOH, 15–40 min, 25°	 (94)	548
	28% H_2O_2, AcOH, 12 h, 20°	$HO_2C(CH_2)_{12}CO_2H$ I (67) + $HO_2C(CH_2)_{11}CO_2H$ II (4) + $HO_2C(CH_2)_9CO_2H$ III (4)	202
	28% H_2O_2, KOH, 12 h, 20°	I (21) + II (16) + III (26)	202
C_{14}			
	35% H_2O_2, H_2SO_4, CH_3OH	 (90)	611
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h	 (88)	613
o-$(C_6H_5CH_2O)C_6H_4CHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 15 h, 25°	o-$(C_6H_5CH_2O)C_6H_4OH$ (91)	578
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h	 (90)	613
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h	 (80)	613
	50% H_2O_2, 85% HCO_2H, 24 h, −5°	 (56)	604
C_{15}			
	MCPBA, CH_2Cl_2, 25°	 (81)	614
	MCPBA, CH_2Cl_2, 25°	 (92)	614
	15% H_2O_2, NaOH, C_5H_5N, 1.5 h, 25°	 (79)	568

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

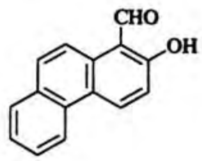
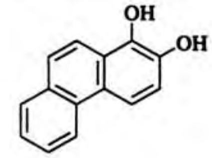
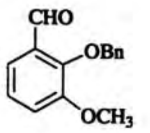
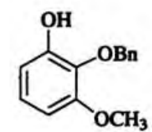
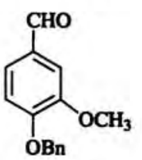
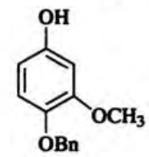
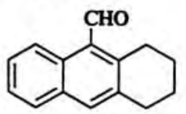
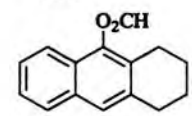
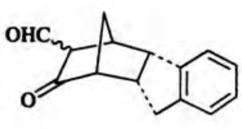
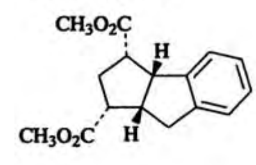
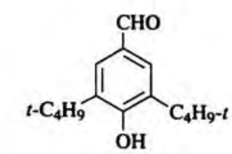
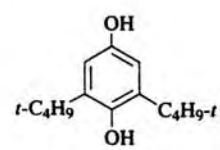
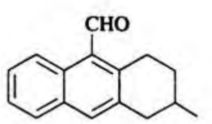
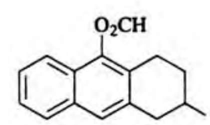
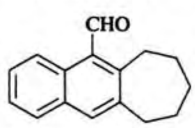
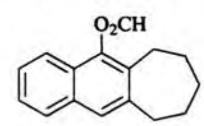
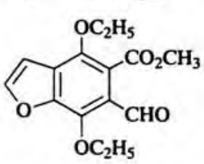
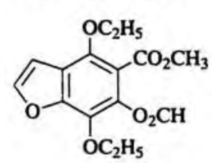
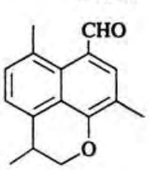
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	15% H_2O_2, NaOH, C_5H_5N, 1 h, 25°		(—)	568
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 72 h, 25°		(79)	578
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 49 h, 25°		(98)	578
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h		(88)	613
	1. 30% H_2O_2, NaOH, 5 h, 25° 2. CH_2N_2, ether		(50)	625
	3% H_2O_2, KOH, 15–40 min, 25°		(87)	548
C_{16}				
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h		(81)	613
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h		(85)	613
	85% MCPBA, $i\text{-}C_3H_7OH$, 12 h, 25°		(—)	582
	MCPBA, CH_2Cl_2, 12 h, 25°	Complex mixture		612
	TFPAA, Na_2HPO_4, CH_2Cl_2, 12 h, 25°	Complex mixture		612
	MCPBA, $ClCH_2CH_2Cl$, $2,6\text{-}(t\text{-}C_4H_9)_2\text{-}4\text{-}HOC_6H_2OH$, 16 h, heat	Complex mixture		612

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

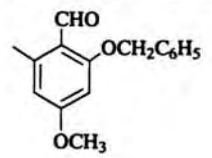
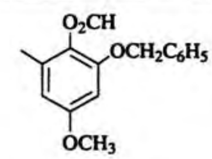
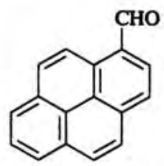
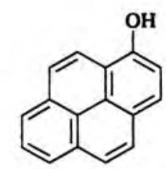
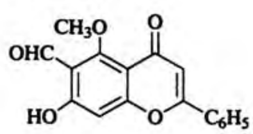
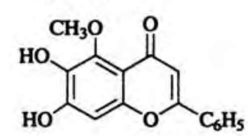
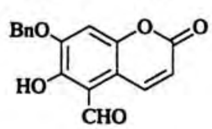
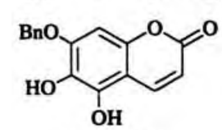
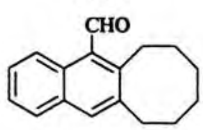
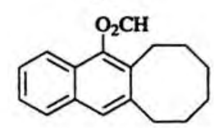
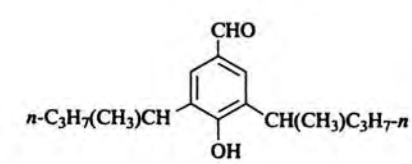
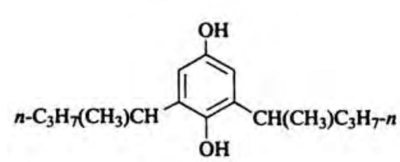
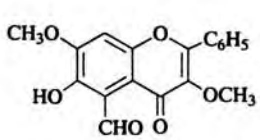
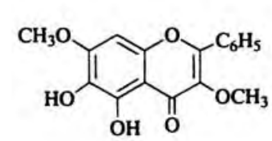
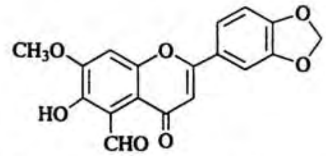
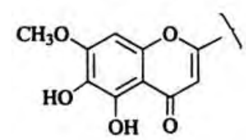
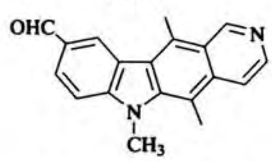
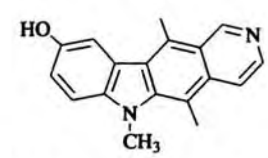
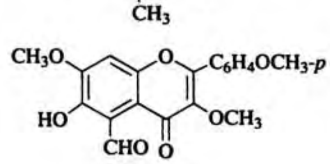
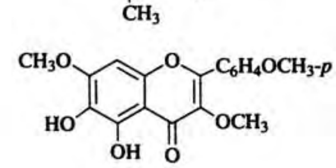
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	85% MCPBA, CH_2Cl_2, 2.5 h, 25°		(85)	596
C_{17}				
	30% H_2O_2, $[2,4\text{-}(O_2N)_2C_6H_3Se]_2$, CH_2Cl_2, 10 h, 25°		(93)	578, 1092
	30% H_2O_2, NaOH, 3 h, 0°		(69)	569
	6% H_2O_2, NaOH, C_5H_5N, 1.25 h, 0–10°		(52)	562
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h		(84)	613
	3% H_2O_2, KOH, 15–40 min, 25°		(46)	548
C_{18}				
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°		(37)	559
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°		(—)	559
	35% H_2O_2, H_2SO_4, CH_3OH		(>90)	611
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°		(46)	559

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

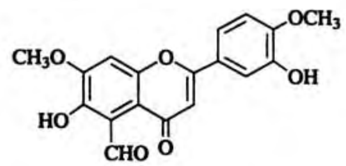
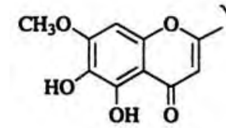
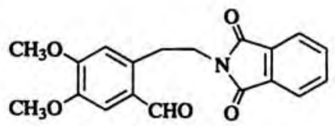
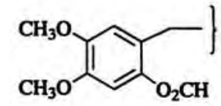
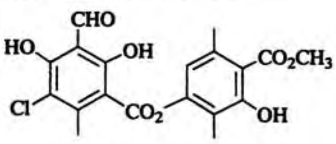
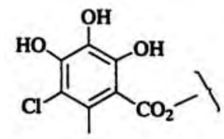
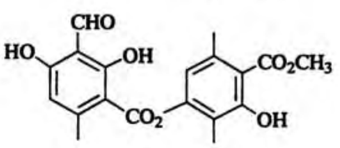
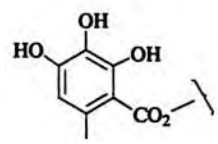
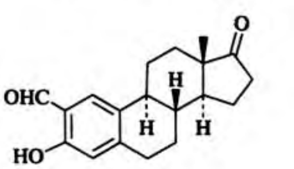
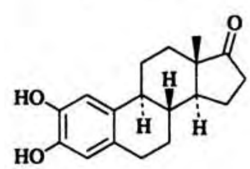
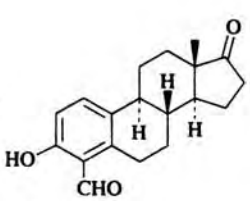
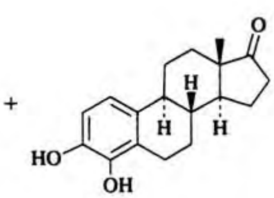
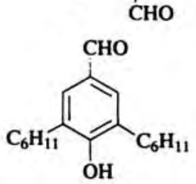
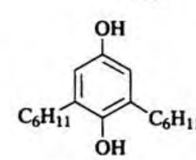
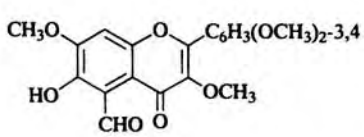
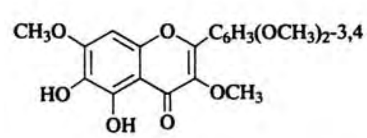
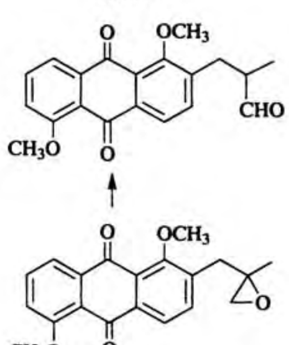
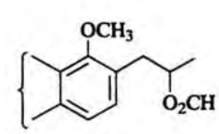
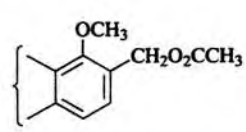
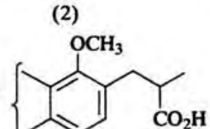
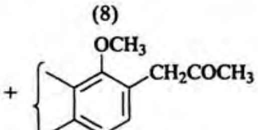
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°	 (—)	560
C_{19}			
	MCPBA, CH_2Cl_2, 6.5 h, 25°	 (60)	597
	6% H_2O_2, NaOH, >1 h, 10°	 (—)	554
	6% H_2O_2, NaOH, >1 h, 10°	 (—)	554
	H_2O_2, diglyme, 6 h, 50°	 (73)	96
+ 		+  (23)	
	3% H_2O_2, KOH, 15–40 min, 25°	 (42)	548
C_{20}			
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°	 (45)	559
	MCPBA, CH_2Cl_2, 3 h, 20°	 (2) +  (8) +  (39) +  (5)	876

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

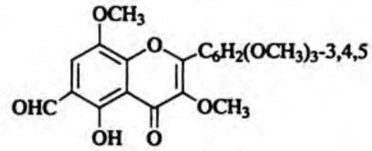
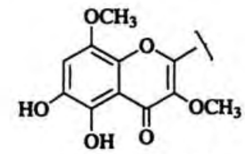
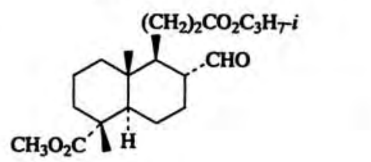
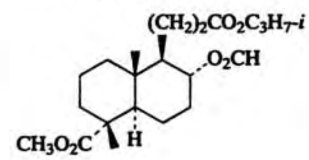
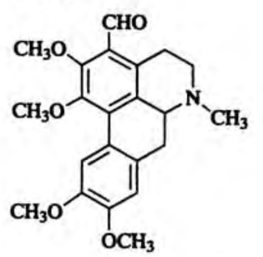
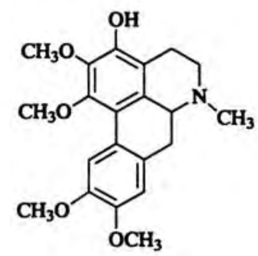
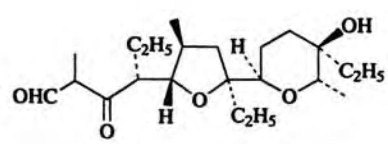
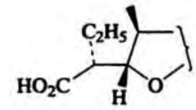
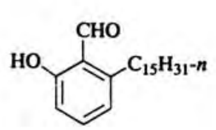
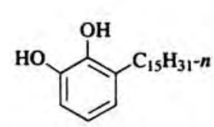
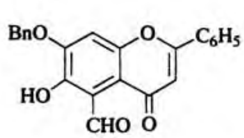
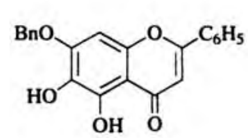
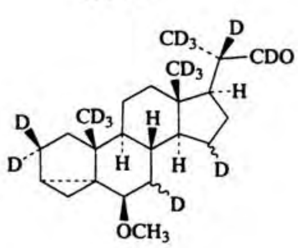
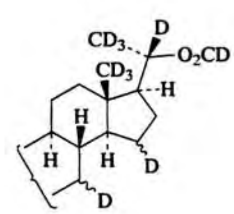
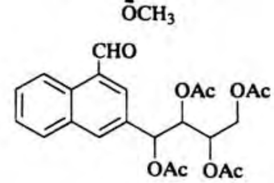
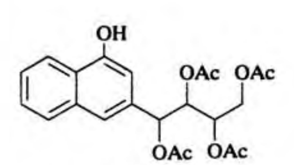
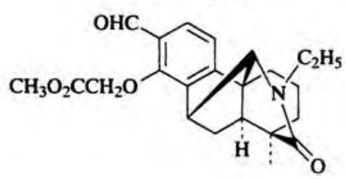
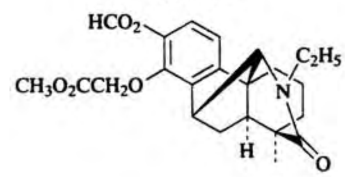
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	6% H_2O_2, NaOH, C_5H_5N, $CHCl_3$, CH_3OH, 2.25 h	 (60)	561
	MCPBA, $KHCO_3$, CH_2Cl_2, 24 h, reflux	 (30)	621
	30% H_2O_2, AcOH, 1.5 h, 45°	 (47)	609
C_{22}			
	TFPAA (90%), Na_2HPO_4, CH_2Cl_2, several min	 (79)	80
	6% H_2O_2, NaOH, 40–50°	 (20)	556
C_{23}			
	1. 6% H_2O_2, NaOH, C_5H_5N, 15 min, 10° 2. 2 h, 25°	 (52)	564
	MCPBA	 (—)	620
	1. MCPBA, CH_2Cl_2, 4–48 h, 25° 2. KF, 4–5 h	 (59)	613
	MCPBA, CH_2Cl_2	 (100)	599

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

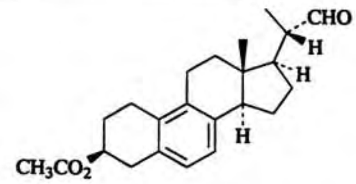
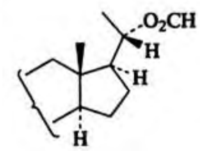
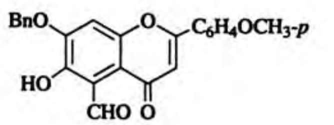
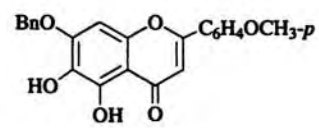
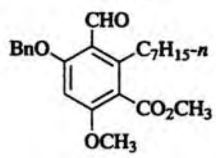
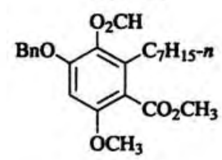
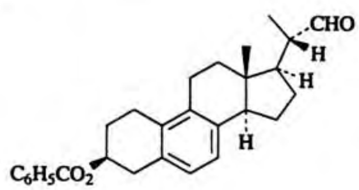
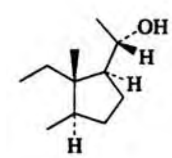
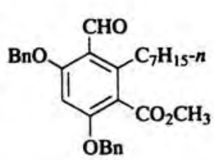
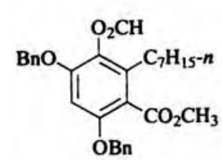
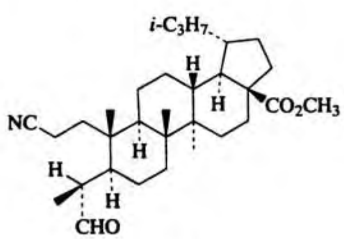
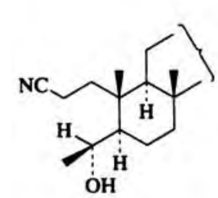
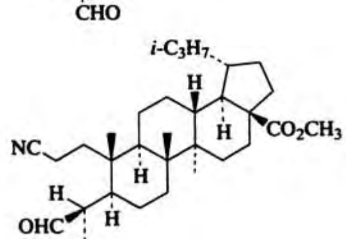
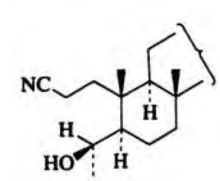
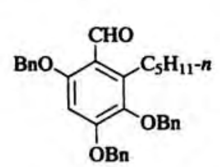
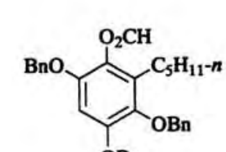
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	30% H_2O_2, HCO_2H, $CHCl_3$, 5 h, 25°		(60–65)	906
C_{24}				
	6% H_2O_2, NaOH, C_5H_5N, 15–20°		(61)	564, 565
	85% MCPBA, CH_2Cl_2, 1 h, 25°		(81)	594
C_{28}				
	1. MCPBA, CH_2Cl_2, 4 h 2. alumina		(29)	906
C_{30}				
	85% MCPBA, CH_2Cl_2, 1 h, 25°		(70)	593, 594
C_{31}				
	MCPBA, CH_2Cl_2, 21 h, 25°		(48)	622
	MCPBA, CH_2Cl_2, 21 h, 25°		(43)	622
C_{33}				
	MCPBA, CH_2Cl_2, 4.3 h, 25°		(84)	595

TABLE VII. REACTIONS OF ALDEHYDES (*Continued*)

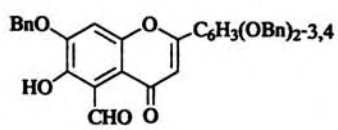
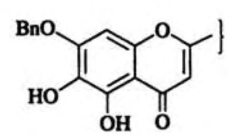
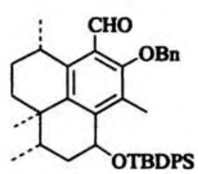
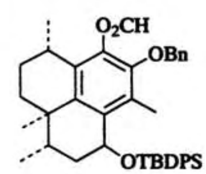
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{37}				
	1. 6% H_2O_2, NaOH, C_5H_5N, 0.5 h, 15–25° 2. 2 h, 25°		(—)	563
C_{41}				
	MCPBA, Na_2HPO_4, $CHCl_3$, 3 h, 20°		(>88)	598

TABLE VIII. REACTIONS OF α, β-UNSATURATED ALDEHYDES

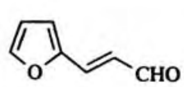
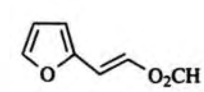
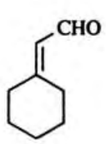
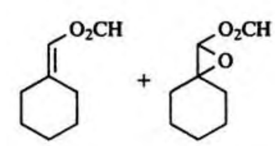
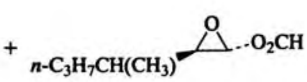
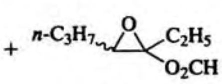
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 27 h, 25°	 (53)	628
C_8			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 23 h, 25°	 (61) + (6) (8)*	628
(*E*)-*n*-$C_3H_7CH(CH_3)CH{=}CHCHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 174 h, 25°	(*E*)-*n*-$C_3H_7CH(CH_3)CH{=}CHO_2CH$ I (45) +(12)*	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 19 h, 25°	I (20)	628
		+  (20)	
n-$C_3H_7CH{=}C(C_2H_5)CHO$	PAA, AcOH, 9 h, 20–25°	*n*-$C_3H_7CH{=}C(C_2H_5)O_2CH$ (50) +  (30)	623
C_9			
(*E*)-$C_6H_5CH{=}CHCHO$	30% H_2O_2, $(C_6H_5Se)_2$, CH_2Cl_2, 54 h, 25°	(*E*)-$C_6H_5CH{=}CHO_2CH$ (68)	628

TABLE VIII. REACTIONS OF α, β-UNSATURATED ALDEHYDES (*Continued*)

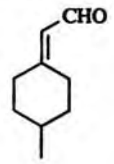
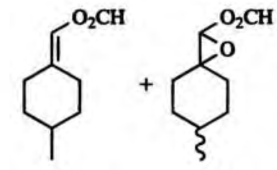
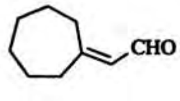
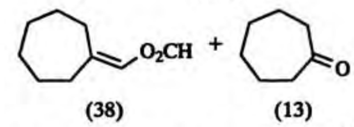
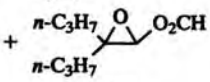
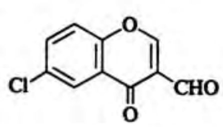
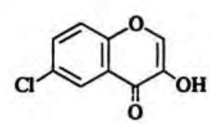
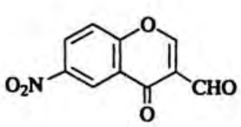
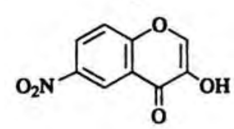
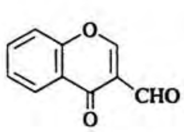
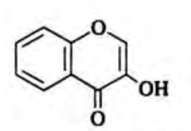
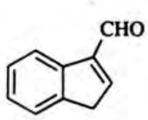
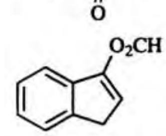
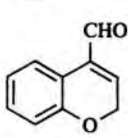
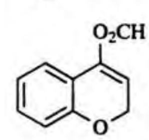
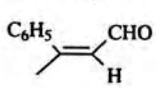
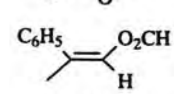
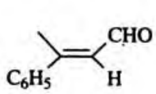
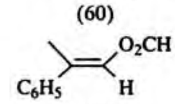
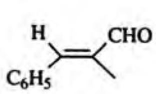
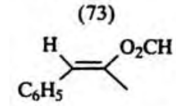
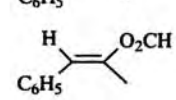
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 32 h, 25°	 (32) (11)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 23 h, 25°	 (38) (13)	628
$(n\text{-}C_3H_7)_2C{=}CHCHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 33 h, 25°	$(n\text{-}C_3H_7)_2C{=}CHO_2CH$ I (64) +  (17)	628
	MCPBA (2 eq), CH_2Cl_2, 39 h, 25°	I (29) + $(n\text{-}C_3H_7)_2COHCHO$ (31) +(7)*	628
C_{10}			
	MCPBA, CH_2Cl_2, 18 h, heat	 (85)	629
	MCPBA, CH_2Cl_2, 24 h, heat	 (80)	629
	MCPBA, CH_2Cl_2, 16 h, heat	 (90)	629
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 22 h, 25°	 (70)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 24 h, 25°	 (59)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 24 h, 25°	 (60) + $C_6H_5COCH_3$ (7) +(5)*	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 15 h, 25°	 (73) + $C_6H_5COCH_3$ (<1) + $C_6H_5C(CH_3)OHCHO$ (12) +(7)*	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 128 h, 25°	 (85)	628
	MCPBA, (2 eq), CH_2Cl_2, 125 h, 25°	 (41) + C_6H_5CHO (24) +(21)*	628
(*E*)-$n\text{-}C_7H_{15}CH{=}CHCHO$	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 190 h, 25°	(*E*)-$n\text{-}C_7H_{15}CH{=}CHO_2CH$ (52)	628

TABLE VIII. REACTIONS OF α, β-UNSATURATED ALDEHYDES (*Continued*)

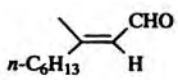
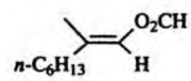
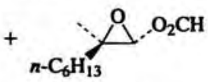
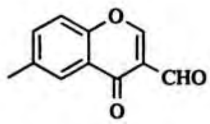
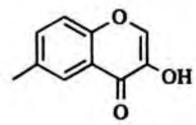
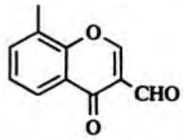
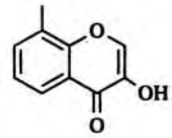
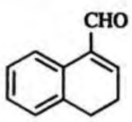
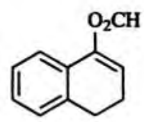
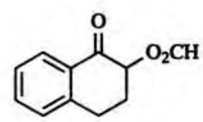
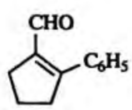
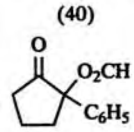
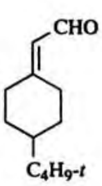
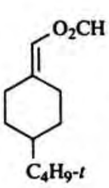
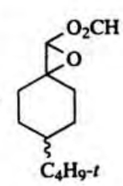
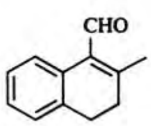
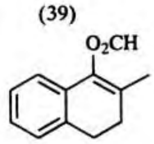
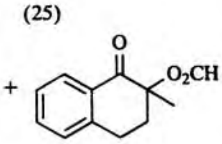
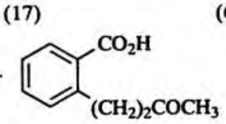
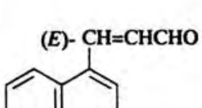
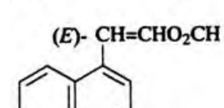
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 22 h, 25°	 (52) +  (10)	628
C_{11}			
	MCPBA, CH_2Cl_2, 24 h, heat	 (85)	629
	MCPBA, CH_2Cl_2, 24 h, heat	 (87)	629
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 97 h, 25°	 (40) +  (20) +(5)*	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 34 h, 25°	 I (60)	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 22 h, 25°	I (46) + $HO_2C(CH_2)_3COC_6H_5$ (26)	
C_{12}			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 19 h, 25°	 (39) +  (25)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 168 h, 25°	 I (17) +  II (69)	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 33 h, 25°	II (78) +  (17)	628
C_{13}			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 168 h, 25°	 I (72) +(8)*	628
	MCPBA (2 eq), CH_2Cl_2, 31 h, 25°	I (54) +(33)*	628

TABLE VIII. REACTIONS OF α, β-UNSATURATED ALDEHYDES (*Continued*)

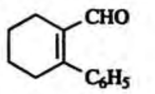
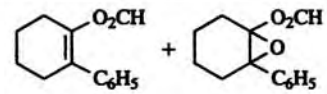
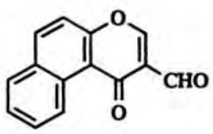
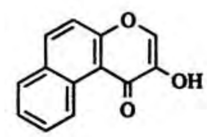
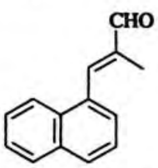
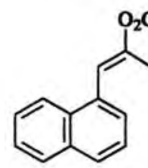
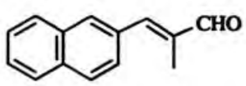
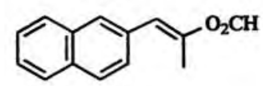
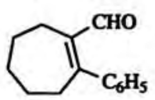
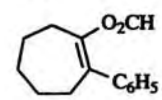
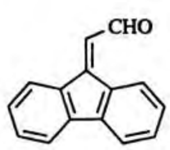
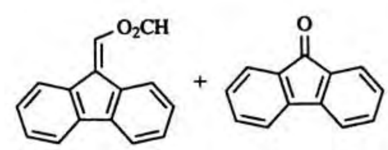
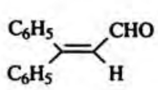
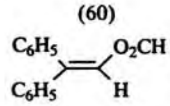
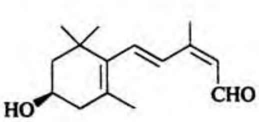
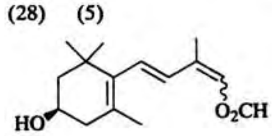
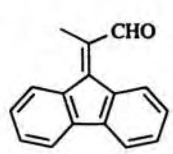
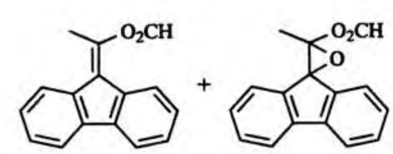
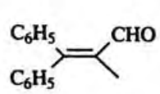
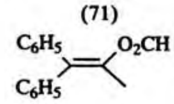
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 105 h, 25°	 (67) (13)	628
C_{14}			
	MCPBA, CH_2Cl_2, 24 h, heat	 (80)	629
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 79 h, 25°	 (94)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 33 h, 25°	 (62)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 124 h, 25°	 (69) +(12)*	628
C_{15}			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 14 h, 25°	 (60) (21) +(7)*	628
	$o\text{-}O_2NC_6H_4SeO_3H$, CH_2Cl_2, 13 h, 25°	 + $(C_6H_5)_2COHCHO$ I (92) II (5)	600, 628
	MCPBA	I + II (28) (5) +(62)*	600
	PAA	 (—)	626
C_{16}			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 123 h, 25°	 (71) (17)	628
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 192 h, 25°	 (87) +(9)*	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 18 h, 25°	I (92)	628

TABLE VIII. REACTIONS OF α, β-UNSATURATED ALDEHYDES (*Continued*)

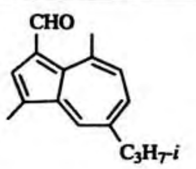
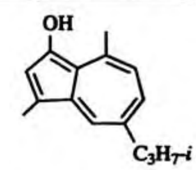
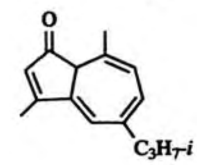
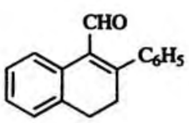
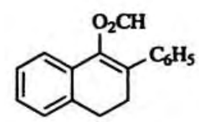
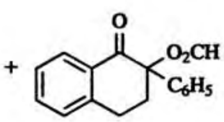
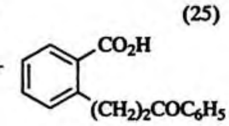
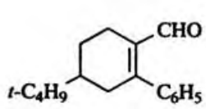
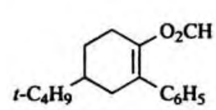
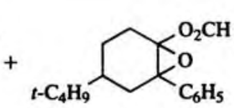
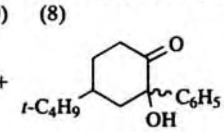
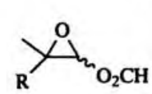
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O_2, NaOH, $HOCH_2CH_2OH$, 25°	 (60)	630
	30% H_2O_2, NaOH, 15 min	 (58)	631
C_{17}			
	30% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 170 h, 25°	 I (66) +  II (25)	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 23 h, 25°	I (18) + II (62) +  (15)	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 11 h, 25°	 I (74) +  II (7)	628
	90% H_2O_2, $(o\text{-}O_2NC_6H_4Se)_2$, CH_2Cl_2, 34 h, 25°	I (60) + II (8) + $HO_2C(CH_2)_2CH(C_4H_9\text{-}t)CH_2COC_6H_5$ (12) +  (11)	628
C_{20}			
(*E*)-$CH_3(R)C{=}CHCHO$ R = $CH_3[CH(CH_3)(CH_2)_3]_3$-	30% H_2O_2, NaOH, or PNPBA, CCl_4, 24 h, 25°	 (98)	627

TABLE IX. PERACID REACTIONS WITH KETALS AND ACETALS

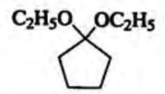
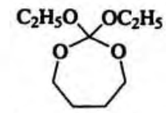
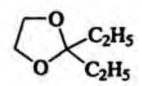
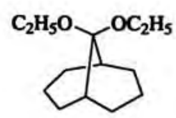
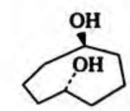
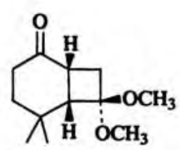
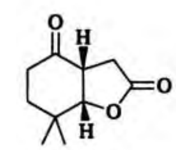
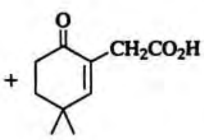
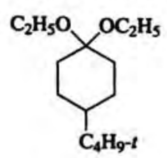
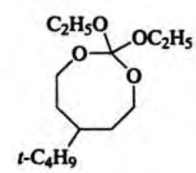
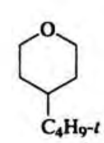
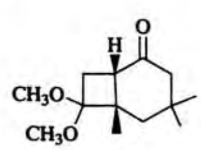
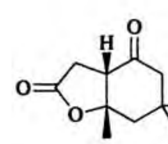
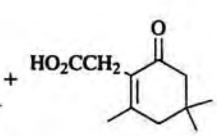
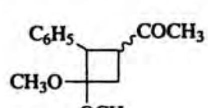
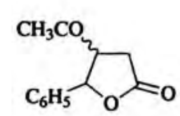
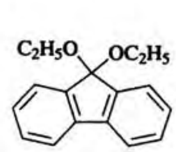
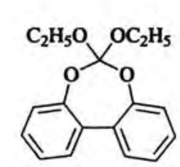
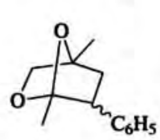
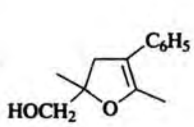
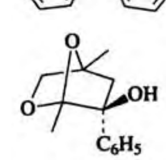
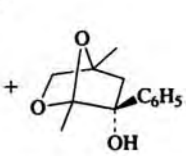
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5			
	MCPBA, CH_2Cl_2, 5 h, 15–30°	 (25)	632
$(C_2H_5)_2C(OC_2H_5)_2$	MCPBA, CH_2Cl_2, 2.5 h, 15–30°	$C(OC_2H_5)_4$ (18) + $(C_2H_5O)_2CO$ (50)	632
	MCPBA, CH_2Cl_2, 72 h, 15–30°	(0)	632
C_9			
	1. MCPBA, CH_2Cl_2, 40 h, 15–30° 2. HCl–H_2O 3. $LiAlH_4$	 (65)	632
C_{10}			
	30% H_2O_2, AcOH, 6–7 h, 25°	 +  (81)	111
	MCPBA, CH_2Cl_2, 9 h, 15–30°	 (30)	632
	MCPBA, CH_2Cl_2, 8.5 h, reflux	 (40)	633
	1. MCPBA, CH_2Cl_2, 13 h, 15–30° 2. HCl 3. $LiAlH_4$	$HO(CH_2)_2CH(C_4H_9\text{-}t)(CH_2)_2OH$ (59)	632
C_{11}			
	30% H_2O_2, AcOH, 6–7 h, 25°	 +  (60)	111
C_{12}			
	30% H_2O_2, AcOH, 6–7 h	 + $C_6H_5CH{=}C(COCH_3)CH_2CO_2H$ (95)	111
C_{13}			
	MCPBA, CH_2Cl_2, 6 h, 15–30°	 (37)	632
 + 	MCPBA, CCl_4, 10 min, 25°	 I +  II I:II = 33:67 (—)	635

TABLE IX. PERACID REACTIONS WITH KETALS AND ACETALS (*Continued*)

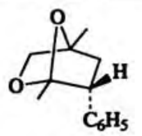
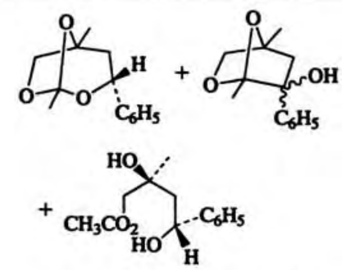
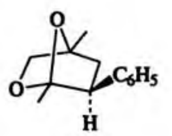
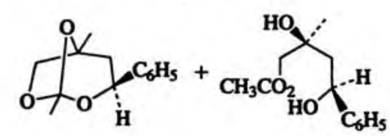
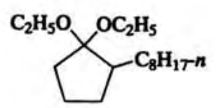
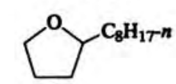
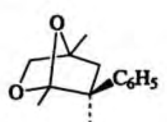
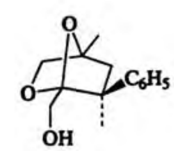
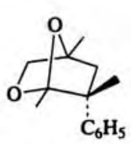
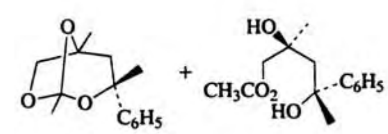
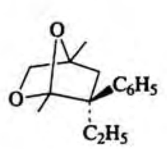
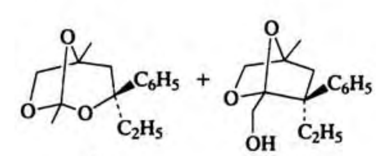
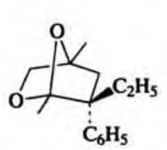
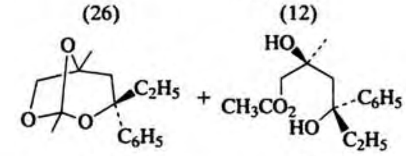
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MCPBA, CH_2Cl_2, 24 h, 0°		(—)	634
	1. 80% MCPBA, CCl_4, 12 h, 25° 2. Florisil, ether	 (53) (26)		634
	MCPBA, CH_2Cl_2, 8.5 h, reflux		(5)	633
C_{14}				
	MCPBA, CCl_4		(46)	634
	MCPBA, CH_2Cl_2, 12 h, 25°	 (48) (25)		634
C_{15}				
	MCPBA, CH_2Cl_2, 12 h, 25°	 + Unknown (26) (12) (29)		634
	MCPBA, CH_2Cl_2, 12 h, 25°	 (—) (9)		634
n-$C_7H_{15}C(OC_2H_5)_2C_7H_{15}$-$n$	1. MCPBA, CH_2Cl_2, 5 h, 15–30° 2. HCl 3. $LiAlH_4$, ether	n-$C_7H_{15}OH$	(75)	632

TABLE X. PERACID REACTIONS WITH NITROGEN DERIVATIVES OF KETONES AND ALDEHYDES

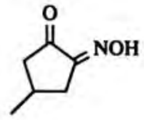
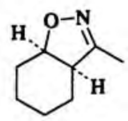
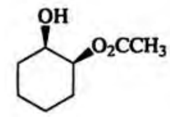
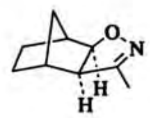
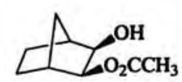
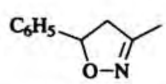
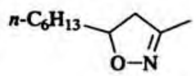
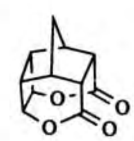
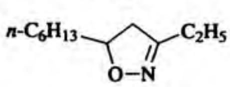
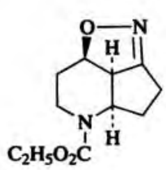
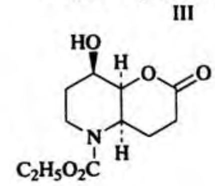
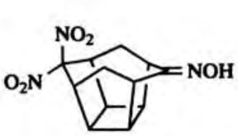
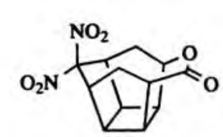
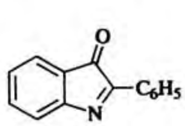
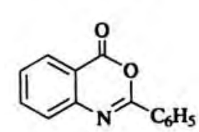
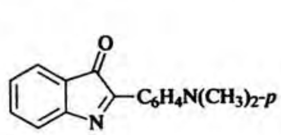
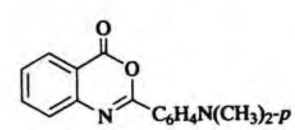
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	TFPAA (90%), Na_2HPO_4, CH_3CN, 1.5 h, 25°	$HO_2CCH_2CH(CH_3)CH_2CO_2H$ major	201
C_8			
	DNPBA, CH_2Cl_2, 17 h, 25°	 (41)	85
C_9			
$C_6H_5COC({=}NOH)CH_3$	TFPAA, Na_2HPO_4, urea, CH_2Cl_2, 1 h, 25°	$C_6H_5CO_2H$ (41) + $C_6H_5CO_2CH(NO_2)CH_3$ (29) + $C_6H_5O_2CCH(NO_2)CH_3$ (5)	201
	1. TFPAA, Na_2HPO_4, CH_2Cl_2, 2 h, 0° 2. 14 h, 5°	 (52)	85
C_{10}			
	DNPBA, TBP, $CHCl_3$, 8 h, heat	$C_6H_5CHOHCH_2O_2CCH_3$ (I) + $C_6H_5CH(O_2CCH_3)CH_2OH$ (II) I:II = 75:25 (67)	85
	DNPBA, Na_2HPO_4, TBP, $ClCH_2CH_2Cl$, 3 h, reflux	n-$C_6H_{13}CH(O_2CCH_3)CH_2OH$ (I) + n-$C_6H_{13}CHOHCH_2O_2CCH_3$ (II) (59) 70:30 Mixture	85
C_{11}			
	90% HNO_3 (fuming), 30% H_2O_2, CH_2Cl_2, 4 h, reflux	 (20)	439
	DNPBA, TBP, $ClCH_2CH_2Cl$, 3 h, heat	$C_6H_5CHOHCH_2CO_2C_2H_5$ (I) + $C_6H_5CHOHCH_2O_2CC_2H_5$ (II) + $C_6H_5CH(O_2CC_2H_5)CH_2OH$ (III) (68 Total)	85
	1. TFPAA, Na_2HPO_4, CH_2Cl_2, 4 h, 0° 2. 18 h, 5°	 (42)	85
C_{12}			
	MCPBA, Na_2HPO_4, urea, CH_3CN, 3 h, heat	 (52)	642
C_{14}			
	85% MCPBA, $CHCl_3$, 12 h, 25°	 (71)	645
C_{16}			
	35% H_2O_2, DMF, 15 h, 25°	 (60)	644

TABLE X. PERACID REACTIONS WITH NITROGEN DERIVATIVES OF KETONES AND ALDEHYDES (*Continued*)

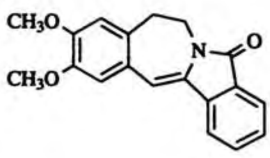
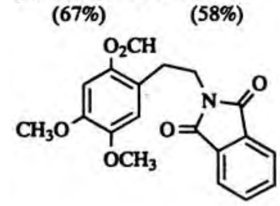
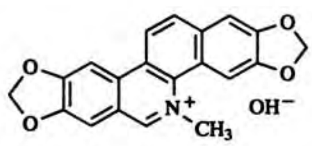
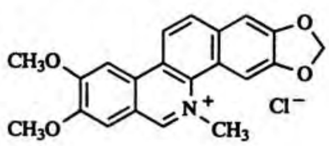
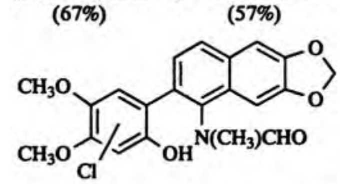
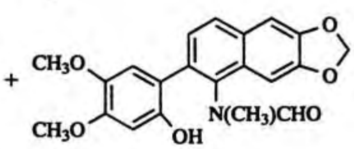
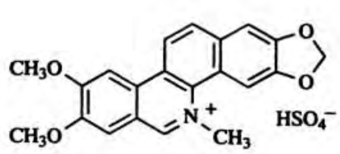
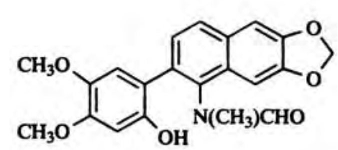
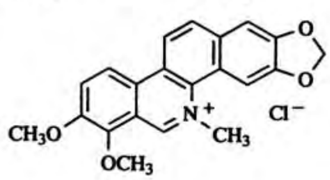
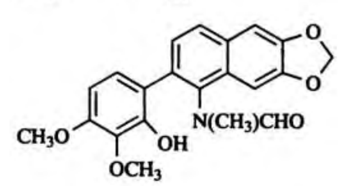
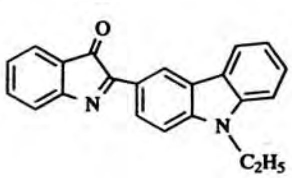
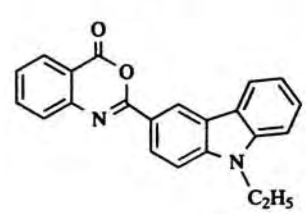
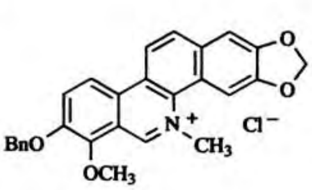
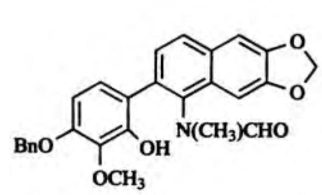
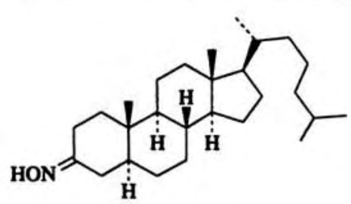
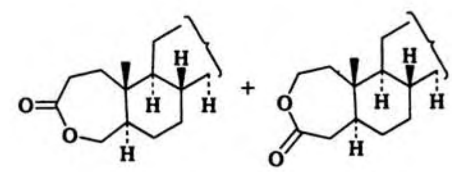
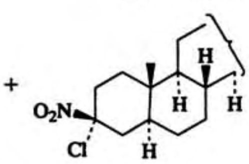
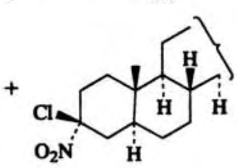
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}			
$(C_6H_5)_2C{=}NCOC_6H_5$	MCPBA, $ClCH_2CH_2Cl$, 1 h, heat	$(C_6H_5CO)_2NH$ (67%) + C_6H_5OH (58%)	646
	MCPBA, CH_2Cl_2, 6.5 h, 25°	 (60)	597
C_{20}			
	MCPBA, TFAA, HMPA, 1 h, 25°	 (79)	647
C_{21}			
$(C_6H_5)(p\text{-}CH_3OC_6H_4)C{=}NCOC_6H_5$	MCPBA, $ClCH_2CH_2Cl$, 1 h, heat	$(C_6H_5CO)_2NH$ (67%) + $p\text{-}CH_3OC_6H_4OH$ (57%)	646
	MCPBA, HMPA, 4 h, 25°	 (39) +  (4)	647, 648
	MCPBA, HMPA, 0.5 h, 70–80°	 (56)	647
	MCPBA, HMPA, 5 h, 40°	 (71)	647, 648
C_{22}			
	35% H_2O_2, DMF, 15 h, 25°	 (53)	644
C_{27}			
	MCPBA, HMPA, 1 h, 40°	 (78)	647

TABLE X. PERACID REACTIONS WITH NITROGEN DERIVATIVES OF KETONES AND ALDEHYDES (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MCPBA, $CHCl_3$, 1 h, reflux	 I + II (20) I:II = 50:50	240
	PAA, $CHCl_3$, 70 min, reflux	I (45) +  (5) +  (7)	643

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