Enantioselective Reduction of Ketones

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1. Introduction

Enantioselective reduction of prochiral ketones is among the most important methods for preparing enantioenriched secondary alcohols, which are important starting materials for a number of enantiopure compounds, including natural products. Various methods for enantioselective reduction of ketones have been developed for producing enantioenriched alcohols. These methods involve the use of both stoichiometric reagents and catalytic reductions. Metal hydride reagents such as lithium aluminum hydride (LAH) and sodium borohydride ($NaBH_4$) are easily modified by enantiopure compounds. For example, binaphthol-modified aluminum hydride reagent (BINAL-H) is a derivative of LAH in which the enantiopure diol 1,1′-bi-2-naphthol and one other alcohol replace three of the hydrogens. This reagent achieves high selectivity in many ketone reductions. The other impressive area of success is the use of enantiopure alkylboranes. The β hydride of enantiopure alkylboranes is delivered selectively, often exclusively, to one face of the carbonyl group of a ketone.

Despite remarkable success with stoichiometric reagents, their important drawback is that at least one equivalent of reagent is required for reduction of the ketone. Thus catalytic processes are desirable for enantioselective ketone reduction as well as for other asymmetric transformations. Hydrogenation and hydrosilylation of ketones are catalyzed by transition metal catalysts. Enantiopure ligand-transition metal complexes can be used as asymmetric catalysts for these reactions. Recent research makes it possible to achieve high enantioselectivity, not only for the reduction of functionalized ketones in which a transition metal can coordinate to an adjacent functional group, but also for simple ketones such as acetophenone. One of the most remarkable catalytic systems described in recent years is borane reduction in the presence of an oxazaborolidine, which contains adjacent donor (nitrogen) and acceptor (boron) sites. Many biologically active compounds have been synthesized by using oxazaborolidine-catalyzed borane reductions of ketones as the key step. Asymmetric reduction with enzymes is another important method. Some baker's yeast mediated ketone reductions have practical applicability.

The following discussion addresses the enantioselective reduction of ketones by various methods including chirally modified hydride reductions, oxazaborolidine catalyzed reductions, Meerwein-Ponndorf-Verley (MPV) reductions, hydrogenations, hydrosilylations, and enzymatic reductions.

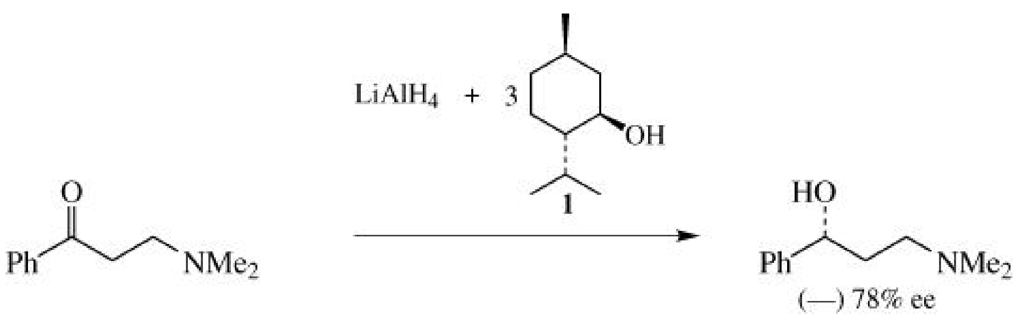
2. Scope and Limitations

2.1. Chirally Modified Lithium Aluminum Hydride Reagents

Since the first enantioselective reduction of ketones with the reagent prepared from LAH and D-camphor was published in 1951, (1) numerous chirally modified LAH reducing agents have been reported. (2-4) Because of their high reactivity, the four hydrogen atoms in LAH can be easily replaced by various chiral modifiers including alcohols, biphenols, amino alcohols, amines, and diamines. Improvements in this method have made it possible to achieve enantioselectivities approaching 100% in the reduction of many prochiral ketones.

2.1.1. Chiral Alcohols

Early studies on LAH reduction using alcohol modifiers such as (–)-menthol or (+)-borneol failed to achieve enantioselective reduction of simple ketones. (5) Monohydroxysaccharide derivatives were also used with only modest success. (6) Although the LAH-menthol (1:1) reagent provided low enantioselectivity in ketone reductions, quite high enantioselectivities were observed when α - and β -dialkylamino ketones were reduced with LAH modified by 3 equivalents of (–)-menthol (**1**). (7) This reagent reduces β -dimethylaminopropiophenone and α -morpholinoacetophenone to the corresponding enantioenriched amino alcohols in 78 and 59% ee, respectively (Eq. 1).



(1)

However, some of these results could not be reproduced by other chemists. (8) It has been suggested that heteroatom substituents in the ketone organize the transition state through coordination of lithium cations, which may enhance the enantioselectivity in LAH-menthol (1:3) reductions. One of the problems with chirally modified LAH reductions is disproportionation of the alkoxyaluminum hydride reagent (Eq. 2). Reduction of the ketone with highly reactive LAH formed by disproportionation gives racemic alcohol product.

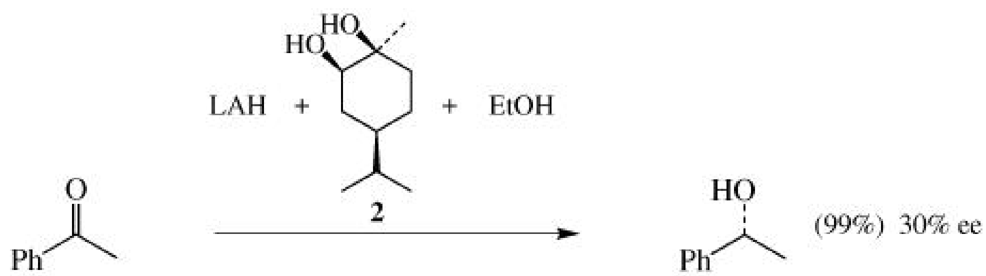
$$LiAlH_4 + R^*OH \longrightarrow 2\,LiAlH_3(OR^*) + H_2$$

$$2\,LiAlH_3(OR^*) \rightleftharpoons LiAlH_2(OR^*)_2 + LiAlH_4 \qquad (2)$$

$$2\,LiAlH_2(OR^*)_2 \rightleftharpoons LiAl(OR^*)_4 + LiAlH_4$$

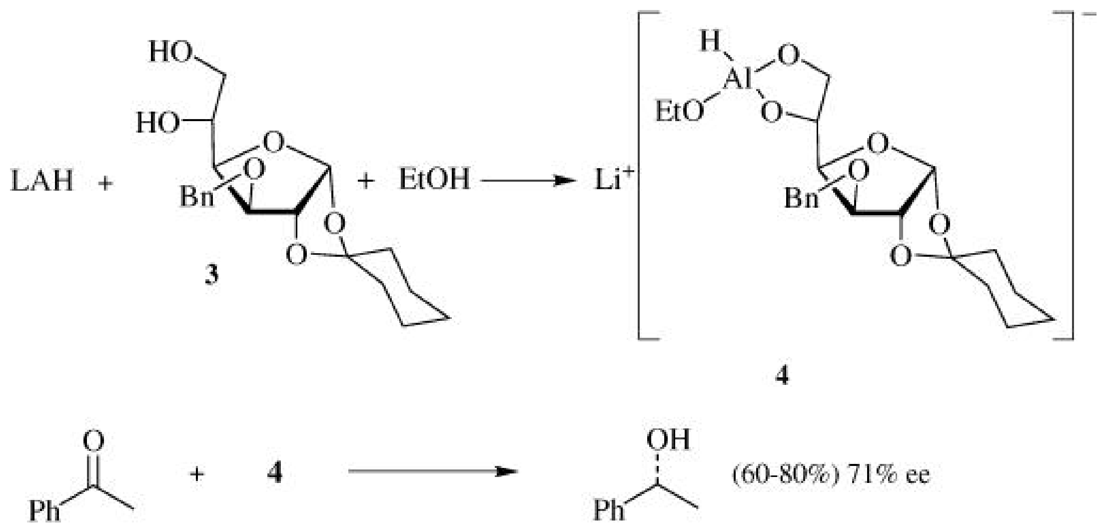
2.1.2. Chiral Diols

In order to minimize disproportionation reactions, diols are used as modifiers. For example, a useful reagent can be prepared from enantiopure chiral diol **2** and LAH followed by addition of ethanol. This reagent reduces acetophenone asymmetrically to give (*R*)-phenethyl alcohol in 30% ee (Eq. 3). (9)



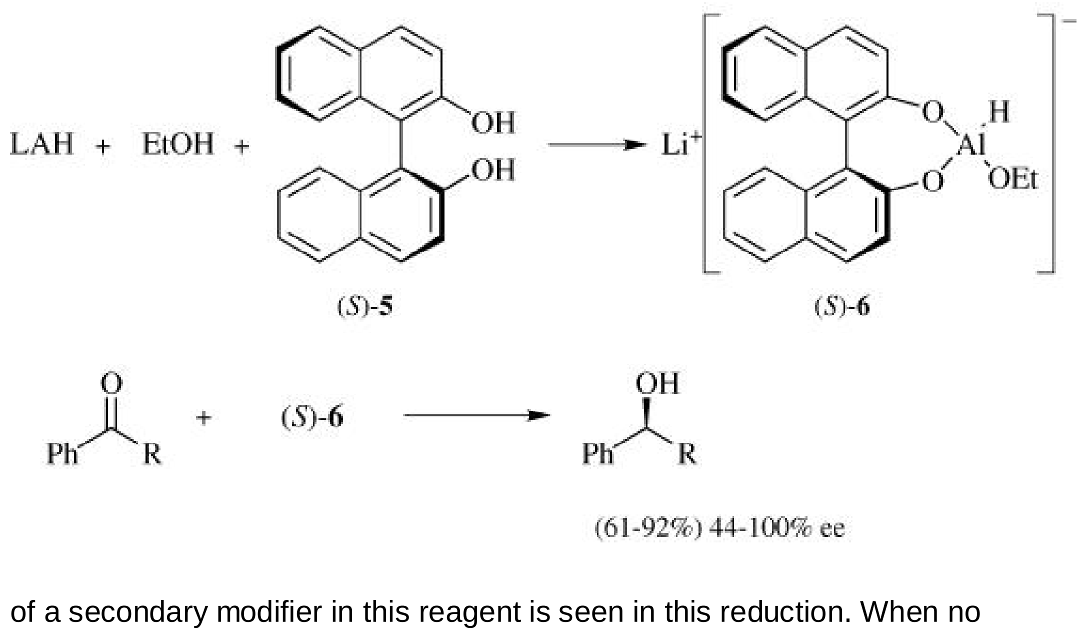
(3)

Another reagent prepared from LAH, *cis*-pinanediol, and benzyl alcohol reduces normethadone in 33% ee. (10) A better result is obtained by the use of D-glucose derivative **3** as a chiral diol modifier. Although the LAH-**3** reagent **4** gives only low enantioselectivity in the reduction of acetophenone, addition of 1 equivalent of ethanol as a secondary modifier improves the enantioselectivity to 71% ee. (11) The structure shown in Eq. 4 is proposed for this reducing agent.



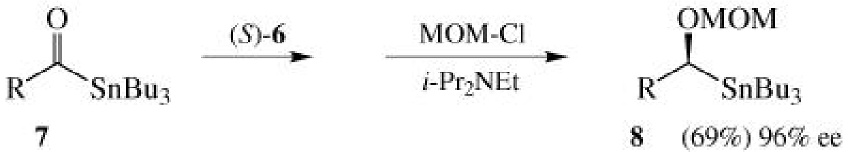
(4)

Many other enantiopure diols have been used as chiral modifiers of LAH. Considerable improvement in enantioselectivity is realized in the reduction of simple aromatic ketones by the use of 2,2′-dihydroxy-1,1′-binaphthyl (**5**). Treatment of LAH with 1 equivalent of ethanol followed by addition of enantiopure binaphthol **5** gives the reducing agent (*S*)-**6** (abbreviated as (*S*)-BINAL-H), which is used in situ for the reduction of prochiral ketones (Eq. 5). The striking effect



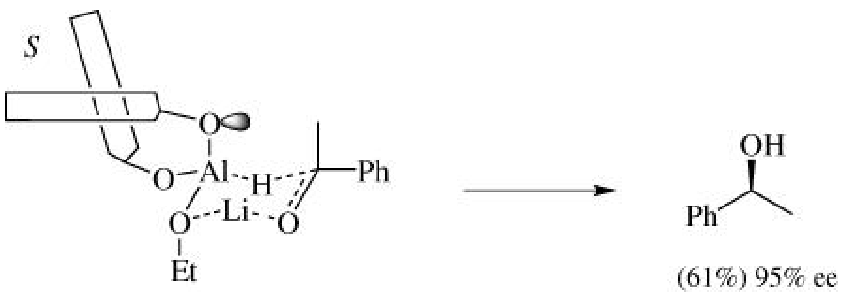
(5)

of a secondary modifier in this reagent is seen in this reduction. When no ethanol is added only 2% ee is obtained in the reduction of acetophenone. However, the same ketone is reduced with (*S*)-**6** in tetrahydrofuran at –100° to give the *S* alcohol in 95% ee, while (*R*)-**6** gives the *R* alcohol. (12, 13) High enantioselectivities are achieved with this reducing agent not only for aromatic ketones but also for α , β -unsaturated ketones and acetylenic ketones (Table I). (14) Prochiral acylstannanes **7** are also reduced, and the resulting α -hydroxystannane is protected to give **8** in up to 96% ee (Eq. 6). (15) In contrast to the reduction of unsaturated ketones, rather low enantioselectivities are obtained in reductions of dialkyl ketones. For example, reduction of 2-octanone with (*S*)-**6** produces (*R*)-2-octanol in 24% ee.



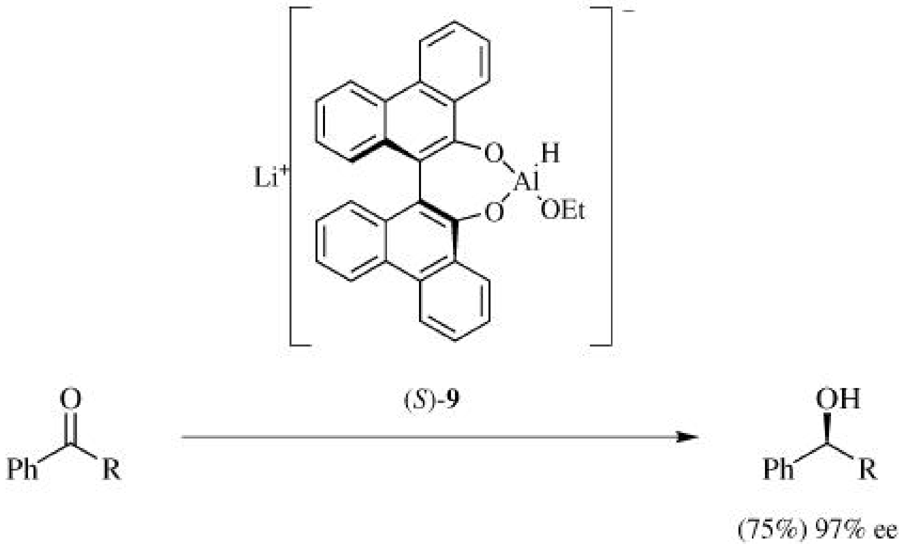
(6)

A chair-like transition state is postulated to explain the results of BINAL-H reductions (Eq. 7). Electronic differences in the substituents on the carbonyl carbon are the principal factors governing the enantiofacial differentiation; steric effects seem to play only a minor role.



(7)

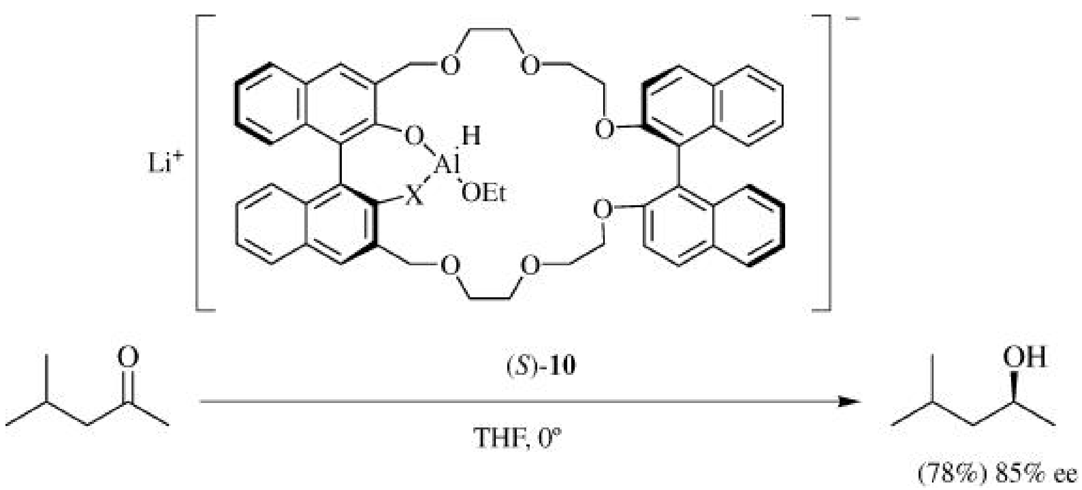
The similar reagent (*S*)-**9** is prepared from LAH, (*S*)-(–)-10,10′-dihydroxy-9,9′-biphenanthryl and ethanol. The enantiopure diol is prepared by stereoselective oxidative coupling of 9-phenanthrol in the presence of (–)-(*R,R*)-1,2-diphenylethylamine-copper(II) complex. This reagent reduces aryl alkyl ketones to *S* alcohols in 97–98% ee at –5° (Eq. 8). (16) The reagent (*S*)-**9** is also



(8)

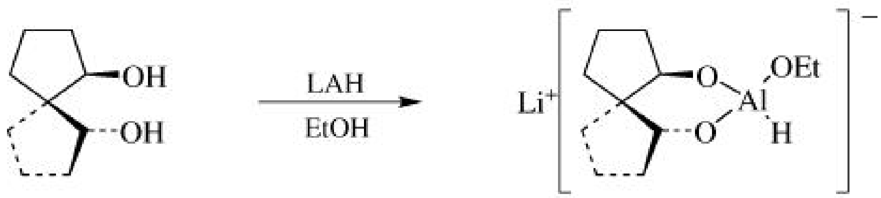
incapable of reducing dialkyl ketones in high enantioselectivity. Reduction of benzyl methyl ketone and isobutyl methyl ketone with **9** gives (*S*)-1-phenyl-2-propanol and (*S*)-4-methyl-2-pentanol in 33 and 21% ee, respectively.

The chiral aluminum hydride reagent **10** exhibits high enantioselectivity in the reduction of prochiral ketones, including aliphatic ketones. (17) The asymmetric reduction of isobutyl methyl ketone gives the corresponding *S* alcohol in 78% yield and in 85% ee (Eq. 9).



(9)

Conformationally rigid diol **11** is another efficient chiral modifier of LAH. Both enantiomers of **11** can be prepared by Cram's procedure (18) and resolved. (19) The LAH complex **12**, formed by treatment of **11** with LAH and ethanol, can be used in the asymmetric reduction of aromatic ketones (Eq. 10). (20) The enantioenriched secondary alcohols are obtained in 70–98% ee (Eq. 11). (20) High enantioselectivity (98% ee) is obtained in the reduction of acetophenone at –80°.

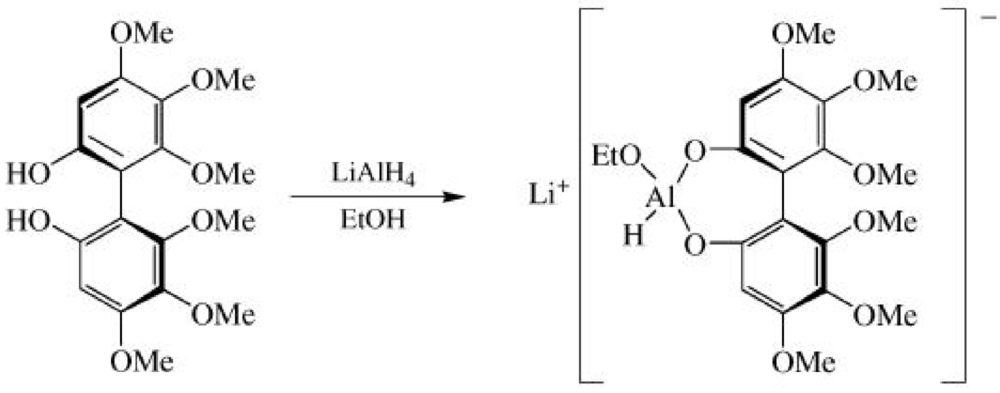


(+)-11 12

(10)

(11)

Enantiopure biphenol **13**, a configurationally stable analog of 2,2 -binaphthol, is also an efficient chiral diol modifier of LAH. (21) Biphenol **13** is prepared by a highly stereoselective biaryl coupling reaction. The chiral reducing agent **14** exhibits high efficiency in the reduction of many prochiral ketones. BINAL-H (**6**) is one of the most efficient asymmetric reducing agents for unsaturated ketones, but gives much lower enantioselectivities with other classes of ketones. In contrast, reducing agent **14** (Eq. 12) (21) gives satisfactory levels of enantioselection with various kinds of ketones including aliphatic ketones (Eq. 13). (21) These results are rationalized by assuming that steric effects play the major role in determining the absolute configuration and optical purity of the product.

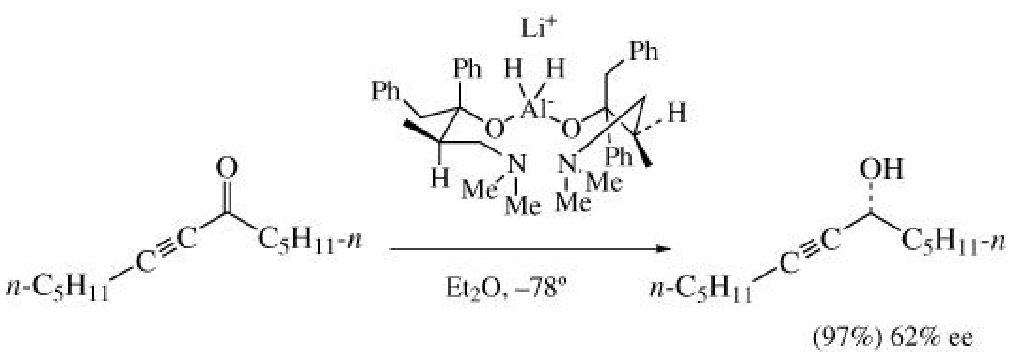


(12)

(13)

2.1.3. Chiral Amino Alcohols

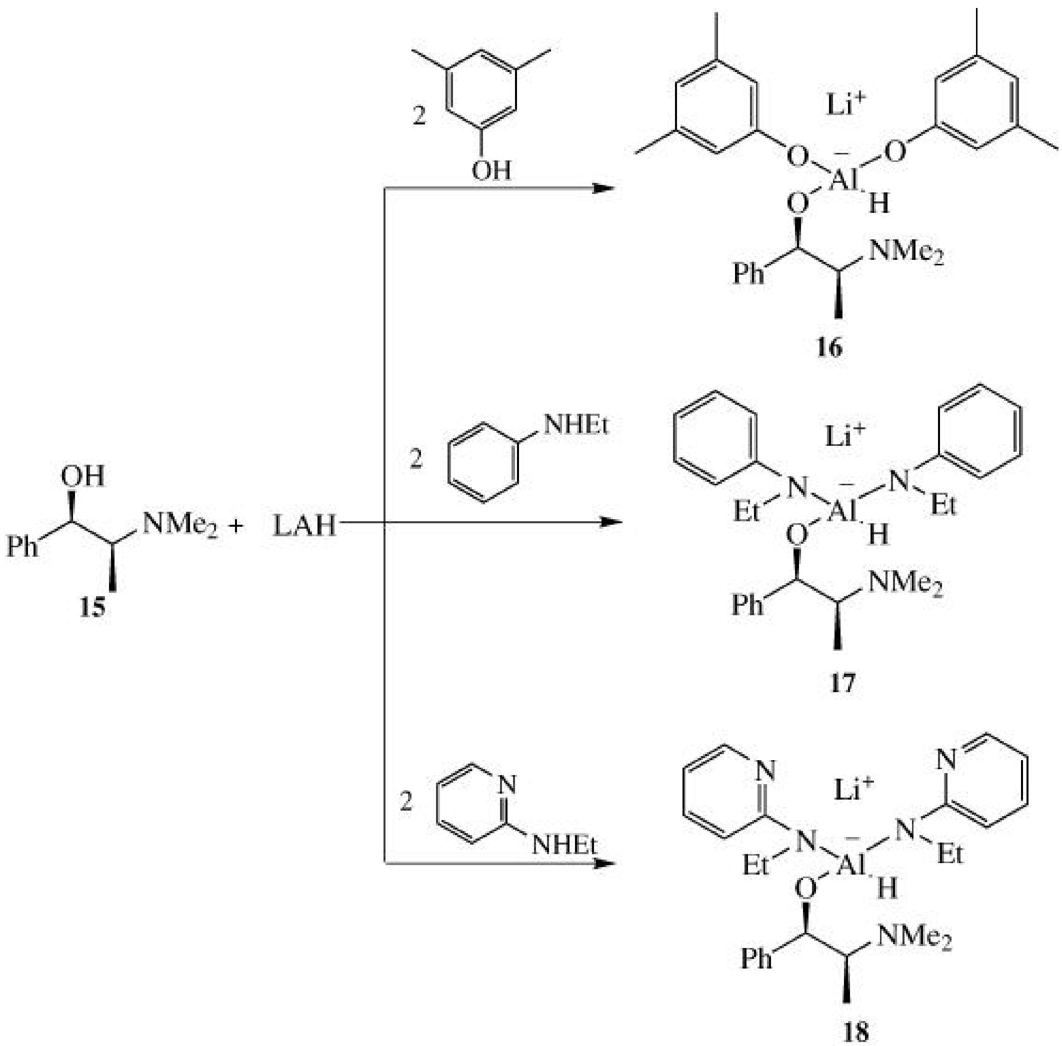
Cinchona alkaloids and commercially available enantiopure amino alcohols are used for various asymmetric syntheses as chiral auxiliaries. The chiral reducing agent prepared from quinine and LAH reduces acetophenone to the alcohol in 48% ee. (22) Use of the enantiopure amino alcohol Darvon alcohol as a chiral auxiliary gives 75% ee in the LAH reduction of acetophenone. (23) Acetylenic ketones are also reduced with this reagent to give propargylic alcohols in useful enantioselectivities (Eq. 14). (24)



(14)

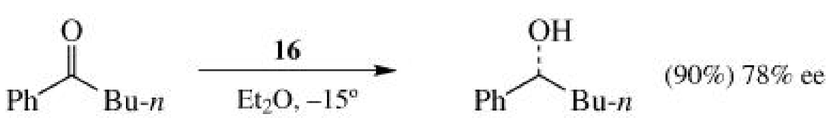
Ephedrine **15** and its derivatives represent another class of readily available enantiopure amino alcohols (Eq. 15). In the reduction of acetophenone the alcohol is obtained in 84% ee with reagent **16**, which was prepared from

(–)-*N*-methylephedrine, 3,5-dimethylphenol, and LAH in the molar ratio of 1:2:1. (25) Various aromatic ketones and acetylenic ketones are reduced with reagent **16** to

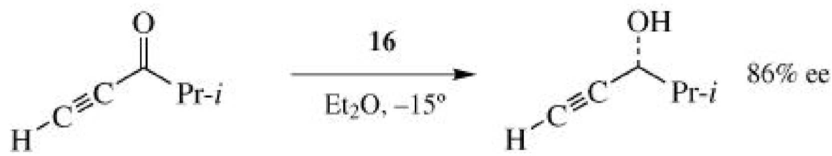


(15)

give the corresponding *R* secondary alcohols in high enantioselectivity (Eqs. 16, 17). (26-28) The ephedrine-derived chiral reducing agent **17** modified by *N*-ethylaniline

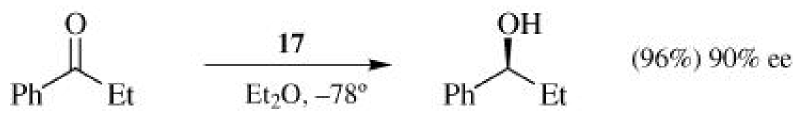


(16)



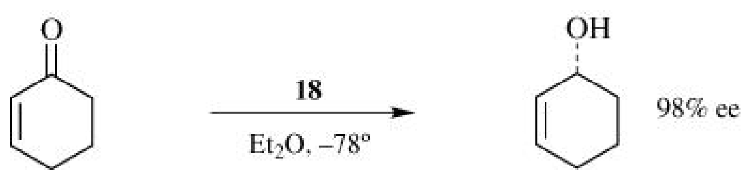
(17)

instead of 3,5-dimethylphenol as in **16** is also efficient in the reduction of aromatic ketones to give predominantly the *S* alcohols (Eq. 18). (29-34) High enantioselectivities



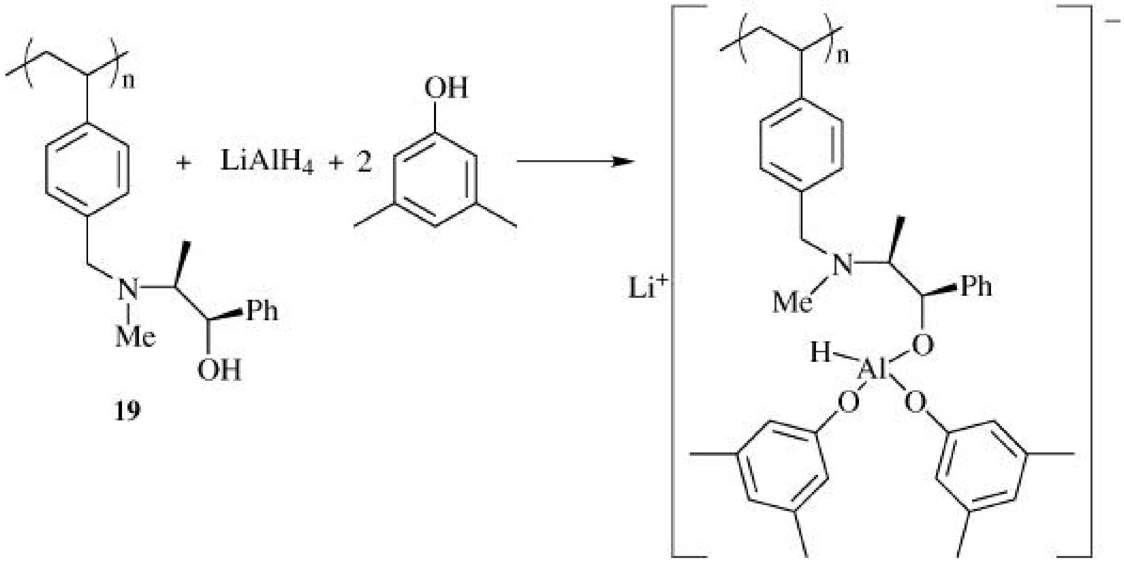
(18)

are attained in the reduction of most α , β -unsaturated ketones except for cyclic enones. The reduction of aliphatic ketones with **16** shows low selectivity, giving less than 50% ee. A similar reagent **18**, modified by a pyridine derivative, provides excellent results in the asymmetric reduction of cyclic enones to *R* alcohols. (35) The reduction of cyclohexen-2-one with the same reagent gives (*R*)-cyclohexen-2-ol in 98% ee (Eq. 19). (35) However only moderate enantioselectivity is obtained in the reduction of acyclic ketones such as acetophenone (54% ee) and propiophenone (46% ee).



(19)

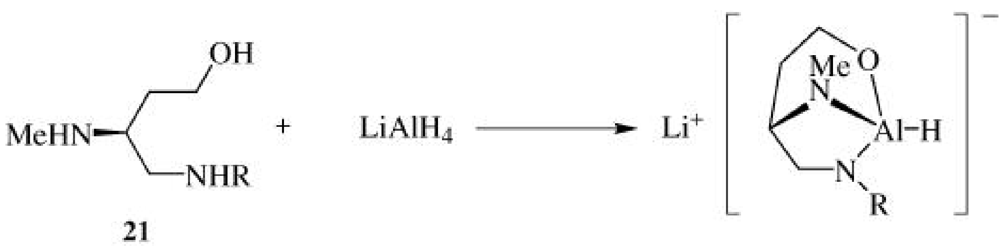
The use of polymer-supported chiral reducing agents is advantageous for asymmetric reductions since the chiral auxiliary can be recycled more easily. A crosslinked polystyrene containing (1*R*,2*S*)-ephedrine bound through nitrogen has been prepared as a polymeric chiral modifier (36) by successive treatment of a solution of LAH with 2 equivalents of 3,5-dimethylphenol and 1 equivalent of polymer **19** (Eq. 20). The resulting complex **20** is used in the reduction of acetophenone to give the enantioenriched alcohol in 79% ee. (36)



20

(20)

Enantiopure diamino alcohols **21** derived from (*S*)-aspartic acid react with LAH to give chiral reducing agents **22** (Eq. 21). (37, 38) Reagent **22a** reduces aromatic ketones to (*S*)-carbinols in 51–88% ee. (38) This reagent also reduces α , β -unsaturated ketones to (*S*)-allylic alcohols, whereas reagent **22b** affords the (*R*)-enantiomers. Although virtually complete enantioselectivity was attained in

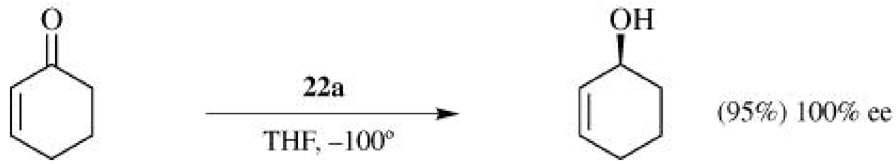


(21)

22

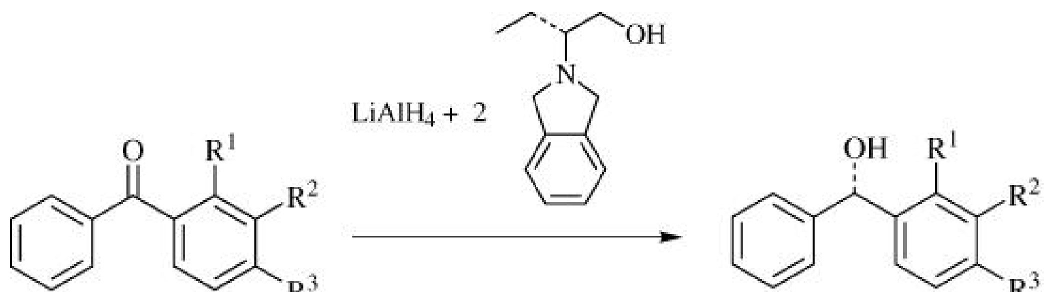
22a, R = Ph
22b, R = 2,6-$Me_2C_6H_3$

the reduction of cyclohexen-2-one by the use of **22a** (Eq. 22), reduction of 3-methylcyclohexen-2-one proceeded in only 28% ee. (37, 38)



(22)

A chiral reducing reagent can be prepared by treatment of LAH with 2 equivalents of (*R*)-(–)-2-(2-isoindolinyl)butan-1-ol. Although this chiral reducing agent shows moderate enantioselectivity in the reduction of simple ketones such as acetophenone, high selectivity is obtained in the reduction of substituted benzophenones in which the carbonyl group carries two large substituents (Eq. 23). Reduction of 2-chlorobenzophenone (**23a**) gives only one enantiomer of the secondary alcohol. (39) However, the 3-chlorobenzophenones **23b** and **23c** lead to markedly lower asymmetric inductions.

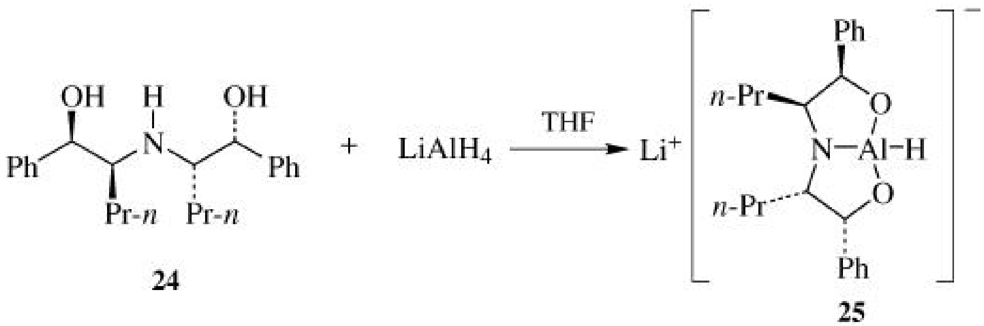


23

(23)

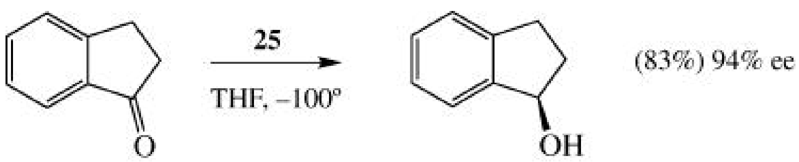
R^1	R^2	R^3	
Cl	H	H	(96%) 100% ee
H	Cl	H	(—) 3% ee
H	Cl	Cl	(—) 8% ee

Enantiopure diethanolamines such as **24** are prepared from enantiopure cyanohydrins and used for the chiral modification of LAH (Eq. 24). (40) Although



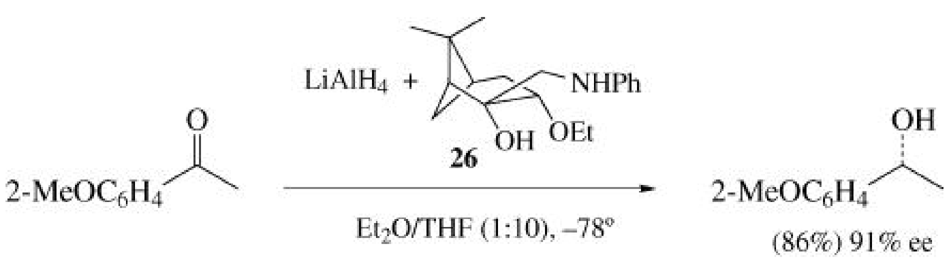
(24)

asymmetric reduction of acetophenone shows moderate selectivity, the reduction of 1-indanone with **25** is achieved in 94% ee (Eq. 25). Recently, a new chiral



(25)

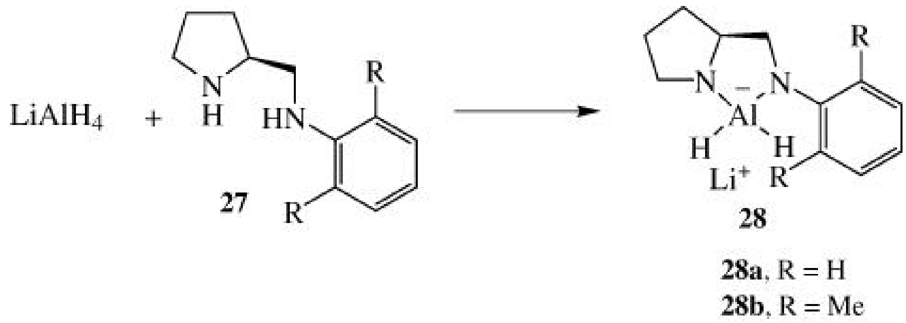
amino alcohol modifier, (1*R*, 2*S*, 3*S*, 5*R*)-(+)-10-anilino-3-ethoxy-2-hydroxypinane (**26**) has been derived from (1*R*)-(–)-myrtenol. The reduction of aryl and alkenyl methyl ketones with LAH modified with **26** affords enantioenriched alcohols in moderate to high enantioselectivities (Eq. 26). (41)



(26)

2.1.4. Chiral Diamines

Enantiopure diamines are also effective chiral auxiliaries for modifying LAH. Asymmetric reduction of prochiral ketones with the reagent **28a** prepared from LAH and (*S*)-2-(anilinomethyl)pyrrolidine (**27**) yields enantioenriched alcohols with the *S* configuration (Eqs. 27, 28). High enantioselectivities



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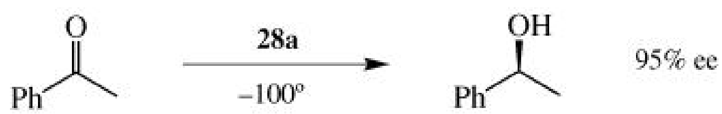
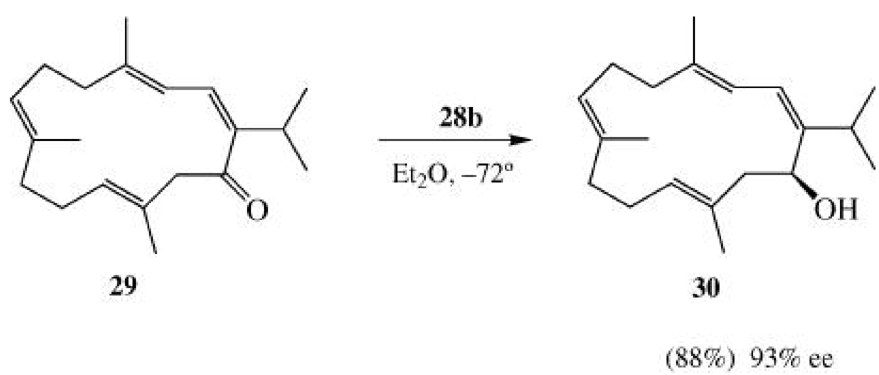


(28)

(90–95% ee) are obtained with this enantiopure diamine modifier in aromatic ketone reductions. (42-44) Acetophenone is reduced with the xylene analog **28b** at –100° to give the *S* alcohol in 95% ee. With aliphatic ketones, asymmetric reduction with **28b** results in low to moderate selectivities (10–40% ee). Use of this reagent in the reduction of macrocyclic enone **29** gives sarcophytol A (**30**), a marine cembranoid, in 93% ee (Eq. 29). A single recrystallization of crude **30** of 93% ee gives enantiomerically pure sarcophytol. (45)



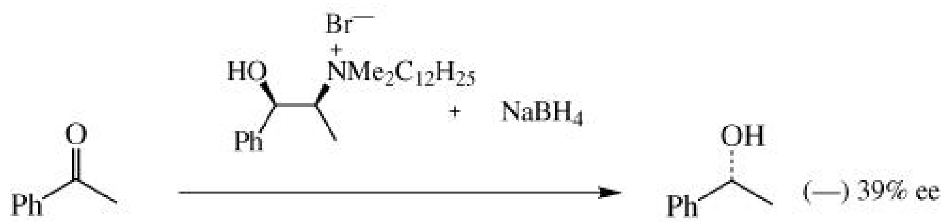
(29)

2.2. Chirally Modified Borohydride Reagents

Various borohydride-based reducing agents have emerged that rival the LAH-derived reagents. There have been several approaches to the modification of borohydride reagents for asymmetric reduction. First, the borohydride anion (BH_4^-) can be modified through the use of chiral counterions. Second, the hydrides can be replaced by chiral modifiers including enantiopure alcohols, carboxylic acids, hydroxy acids, and amino alcohols. Polymer-supported chiral modifiers are also important as recyclable modifiers.

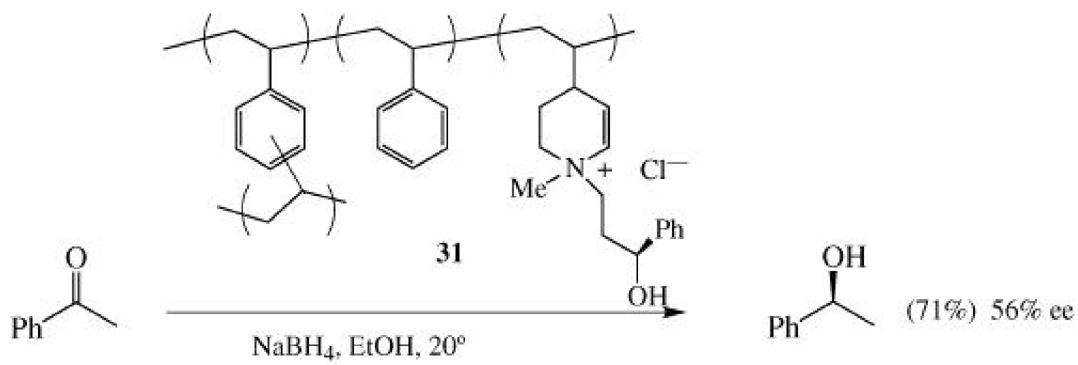
2.2.1. Chiral Quaternary Ammonium Salts

Because of the poor solubility of sodium borohydride in usual organic solvents, reductions are usually performed in aqueous or alcoholic solution. One approach to asymmetric reduction is to replace the sodium cation with an enantiopure quaternary ammonium ion, which serves as a phase transfer catalyst (PTC) in organic solvents. However, enantioselectivities obtained by this approach are generally low (Eq. 30). (46, 47) Bovine serum



(30)

albumin also acts as a chiral modifier in the $NaBH_4$ reduction of ketones. (48) Propiophenone is reduced asymmetrically by this system to (*R*)-1-phenylpropanol in 78% ee. Polymer-supported chiral quaternary ammonium salts also have been synthesized and used for the asymmetric reductions. In the presence of polymer **31**, $NaBH_4$ reduces acetophenone in 56% ee (Eq. 31). (49)



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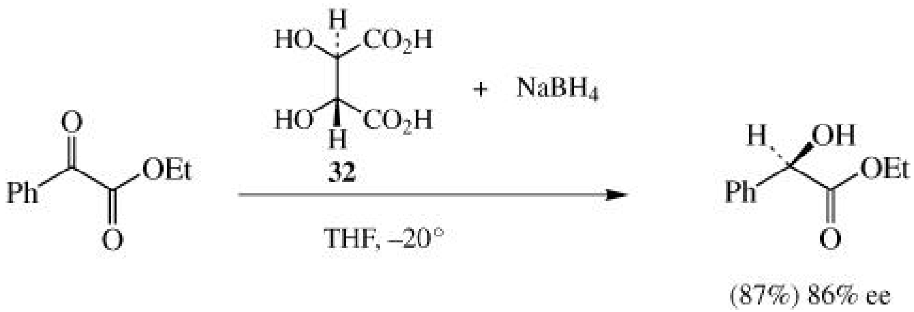
2.2.2. Chiral Carboxylic Acids

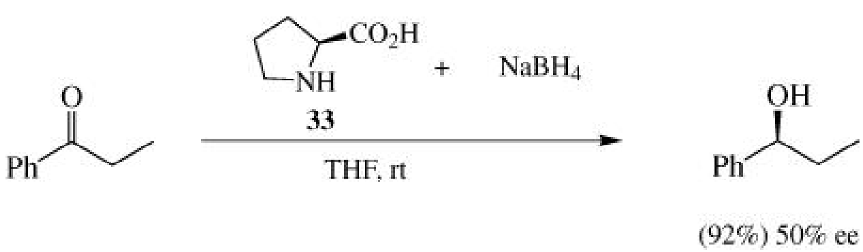
Carboxylic acids react with $NaBH_4$ to form acyloxyborohydrides with liberation of hydrogen; thus enantiopure carboxylic acids are potential chiral modifiers of $NaBH_4$. The first examples reported, using (1*R*, 3*R*)-(+)-camphoric acid and (2*R*, 3*R*)-(+)-tartaric acid, afforded low enantioselectivities. (50) Although $NaBH_4$ in combination with tartaric acid **(32)** reduces simple ketones such as acetophenone and 2-heptanone to the corresponding alcohols with only low enantioselectivities, this reagent reduces α - and β -keto esters to hydroxy esters in high yield with good enantioselectivities (68–86% ee) as illustrated in Eq. 32. (51) Several other enantiopure hydroxy acids, including (*S*)-(+)-lactic,



(32)

(*S*)-(–)-malic, (*S*)-(+)-mandelic and (*R*)-(–)-camphanic acids, are used as modifiers of $NaBH_4$. However, asymmetric reduction of ethyl acetoacetate results in low enantioselectivities with these reagents. (52)

α -Amino acids are also efficient chiral modifiers of $NaBH_4$. The chiral reducing agent prepared from $NaBH_4$ and (*S*)-proline (**33**) reduces propiophenone with 50% ee (Eq. 33). This reducing agent has been applied to the synthesis of the cardiotonic agent **34** (Eq. 34). (53)



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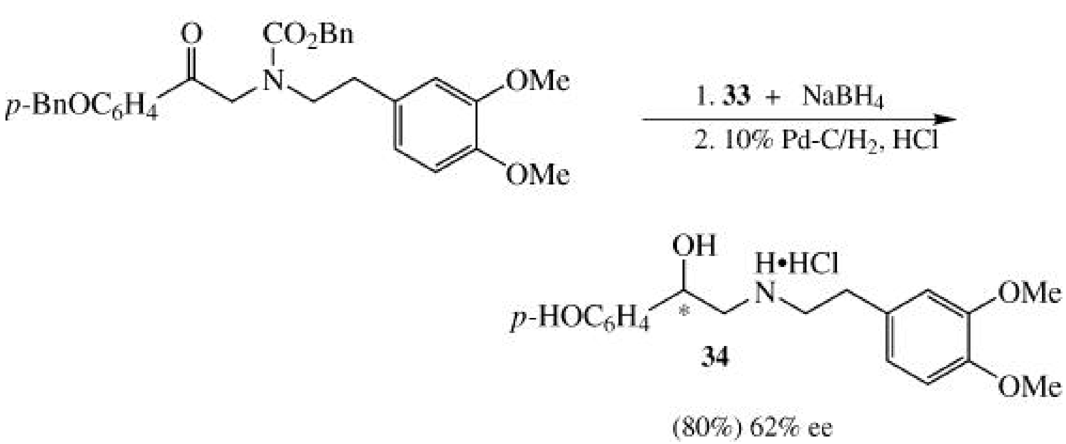
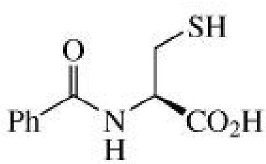


(34)

Higher selectivities have been obtained by using L-cysteine and L-cystine derivatives as chiral modifiers of lithium borohydride ($LiBH_4$). The mixture of (*R*)-*N*-benzoylcysteine (**35**) with $LiBH_4$ in the presence of *tert*-butyl alcohol reduces aromatic ketones in high yields with high enantioselectivities (57–92% ee) (Eq. 35). (54-59) In the case of **36**, the disulfide linkage is presumably cleaved by



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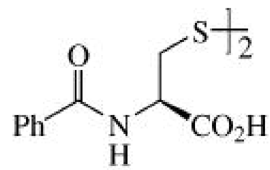

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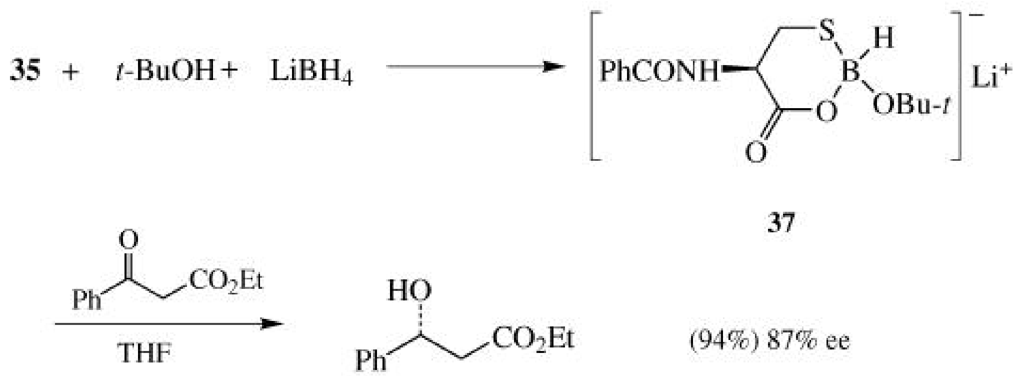
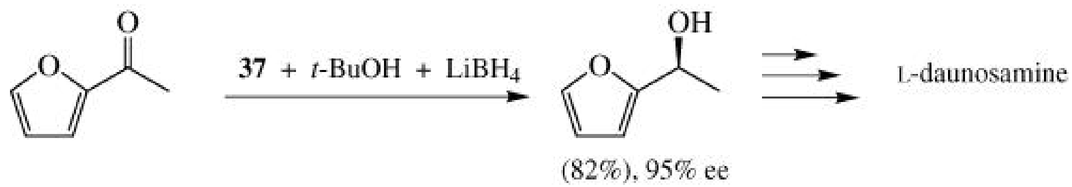


(35)

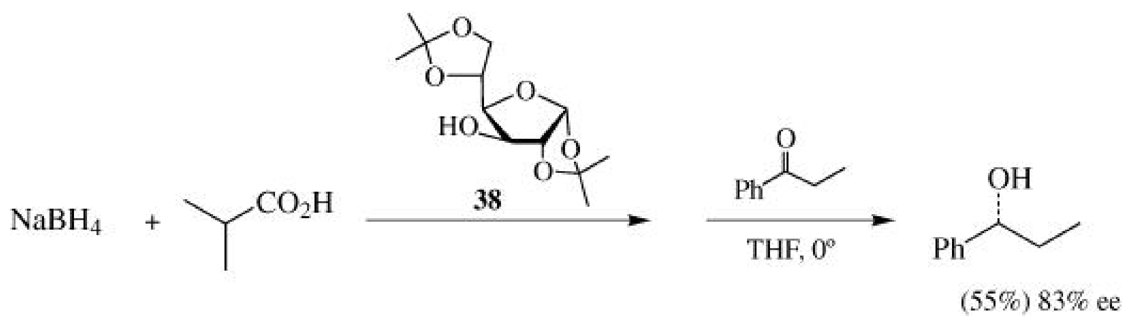
$LiBH_4$ to form the same complex **37**. The chiral reducing agent $LiBH_4$-**36**-*t*-BuOH can also be used for the reduction of functionalized ketones. Reduction of α -halo ketones and β -halo ketones gives halo alcohols that can be tranformed into enantioenriched epoxides and oxetanes, respectively. (60, 61) Enantioenriched α -and β -amino alcohols are obtained from α - and β -amino ketones with high enantioselectivity. (62) β -Keto esters with active methylene groups can be reduced to enantioenriched β -hydroxy esters without any side reactions. (58) The same reagent reduces 2-acetylfuran to acid-labile (*S*)-1-(2-furyl)ethanol, which can be transformed into L-daunosamine (Eq. 36). (63) The chiral auxiliary used for this reduction can be easily removed with alkali, allowing the synthesis of acid-labile chiral alcohols.



(36)

2.2.3. Acids and Chiral Alcohols

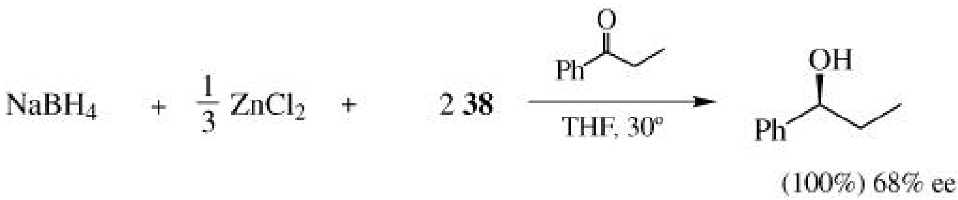
In contrast to chiral acids, enantiopure alcohols are not suitable modifiers of $NaBH_4$ since they are normally inert to $NaBH_4$. Asymmetric induction in the reduction of acetophenone with $NaBH_4$ in the presence of the enantiopure alcohol 1,2,5,6-di-*O*-isopropylidene- α-D-glucofuranose (**38**) is low (18% ee). (64) However, addition of an achiral carboxylic acid to this system dramatically increases enantioselectivity. (65) Reaction of a carboxylic acid with $NaBH_4$ forms an acyloxyborohydride which can be used for various selective reductions. (66) The acyloxyborohydride obtained from reaction of an achiral carboxylic acid with $NaBH_4$ reacts with an enantiopure alcohol to yield a chiral reducing agent; $NaBH_4$-isobutyric acid-**38** is an efficient asymmetric reducing agent for aromatic ketones, giving the corresponding secondary alcohols in up to 83% ee (Eq. 37). (65) Enantiopure diols derived from (*R*)-(+)-camphor are also



(37)

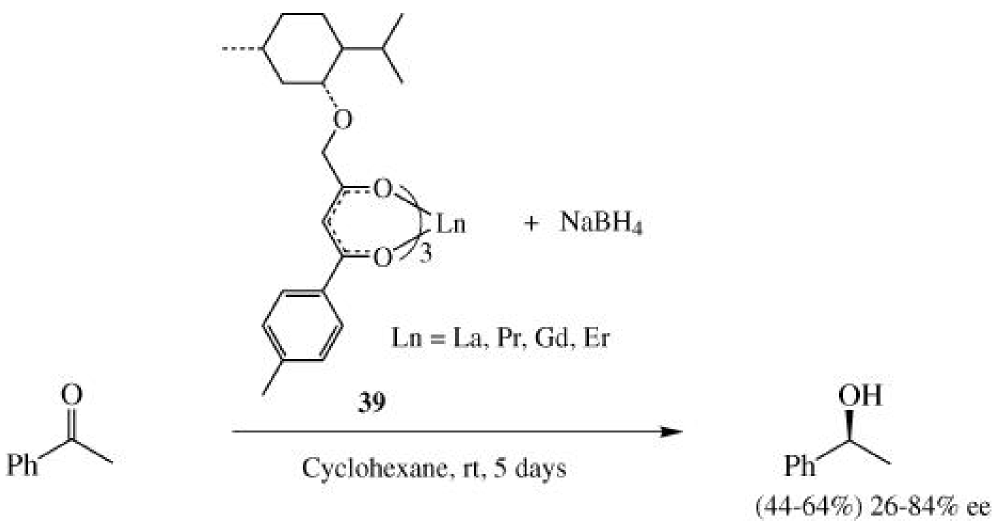
used as chiral modifiers. (67) The reagent derived from hydroxy monosaccharide **38** and $NaBH_4$ is reported to reduce benzylacetone to the corresponding alcohol in 81% yield and 62% ee without acid additives. (68)

Not only carboxylic acids, but also Lewis acids markedly influence the reducing ability of $NaBH_4$. A combination of $ZnCl_2$, $NaBH_4$ and **38** reduces aromatic ketones quantitatively to enantioenriched alcohols. The molar ratio of $ZnCl_2$, $NaBH_4$ and **38** markedly affects the enantioselectivity; the ratio [$ZnCl_2$]:[$NaBH_4$]:[**38**] = 1:3:6 has provided the best result of 68% ee with quantitative yield in the reduction of propiophenone (Eq. 38). (69) Lewis acidmodified $NaBH_4$ can also be used for the reduction of oximes to give enantioenriched primary amines with high enantioselectivity. (70, 71)



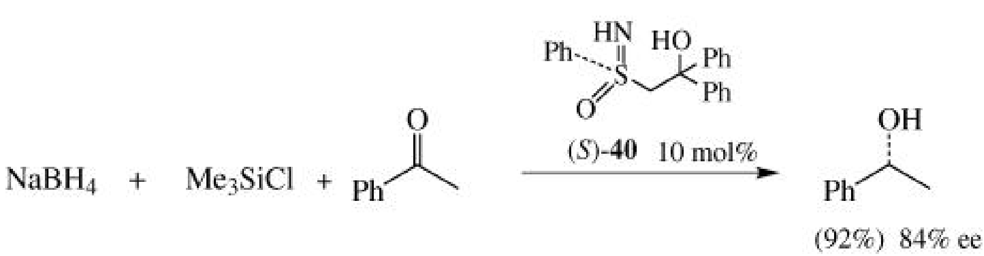
(38)

Although $NaBH_4$ alone does not reduce ketones to alcohols in cyclohexane, in the presence of enantiopure lanthanide complexes **39** the asymmetric reduction of acetophenone proceeds in up to 84% ee (Eq. 39). (72)



(39)

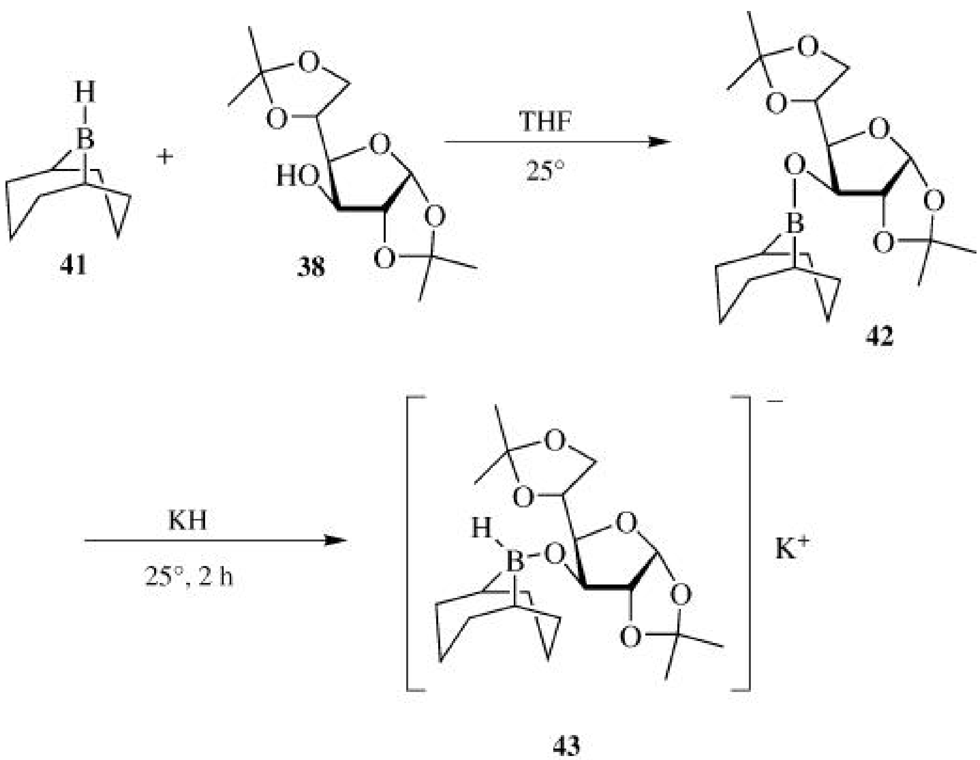
A mixture of $NaBH_4$,Me_3SiCl and an enantiopure ligand can be used for the asymmetric reduction of ketones. In the presence of 10 mol% of enantiopure β -hydroxysulfoximine **40**, complete reduction of acetophenone occurs smoothly at room temperature, and (*R*)-1-phenylethanol is obtained in 92% yield with 84% ee (Eq. 40). (73)



(40)

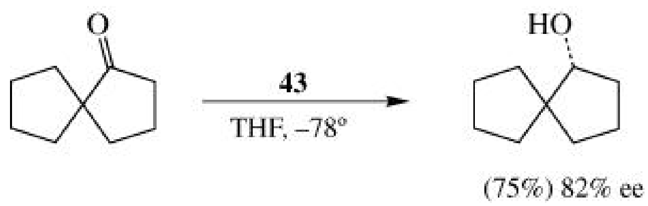
2.2.4. Chiral Alcohols

Metal alkoxyborohydrides can be prepared by treatment of boronic esters with metal hydrides. A series of enantiopure boronic esters has been synthesized by reaction of 9-borabicyclo[3.3.1]nonane (9-BBN) (**41**) with several readily available enantiopure alcohols. (74) An enantiopure boronic ester **42** can then be treated with excess potassium hydride to provide chiral borohydride **43** (Eq. 41), which is an efficient reducing agent for aromatic ketones and α-keto



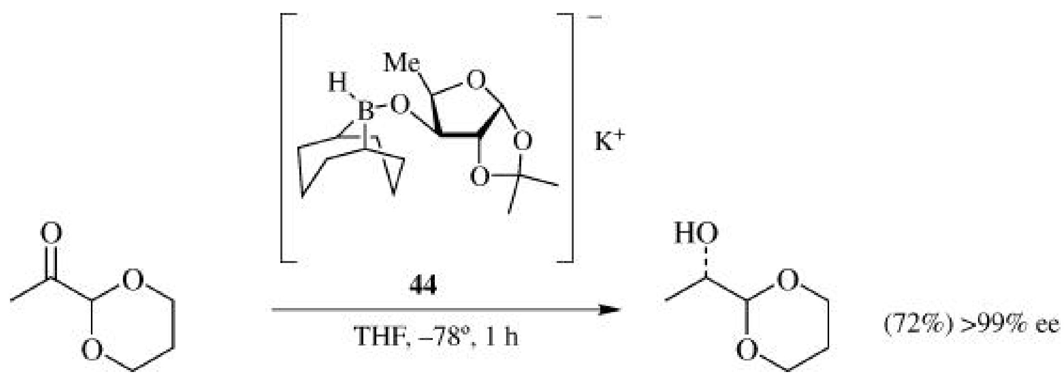
(41)

esters. (75,75a) The reduction of unhindered aliphatic ketones is much less favorable, achieving only limited enantioselectivities. In the reduction of a series of relatively hindered aliphatic and alicyclic ketones, the *R* alcohols are obtained in high enantioselectivity: 70% ee for pinacolone, 84% ee for 2,2-dimethylcyclopentanone, and 82% ee for spiro[4.4]nonan-1-one (Eq. 42). The reduction of α -amino ketones with this reagent at –78° affords *S* amino alcohols. (76)



(42)

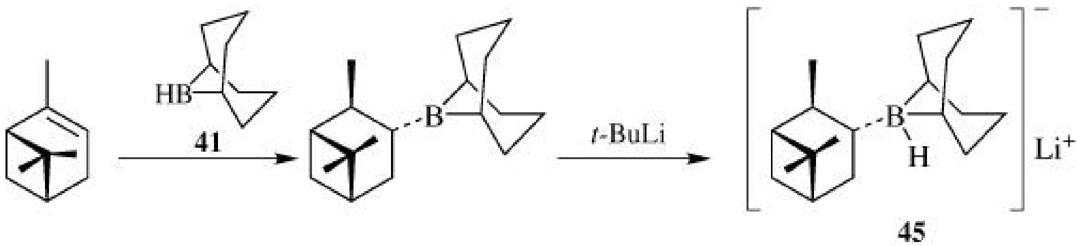
A similar reagent derived from 1,2-di-*O*-isopropylidene-5-deoxy- α -D-xylofuranose gives higher enantioselection in the asymmetric reduction of various ketones. (77) Chiral borohydride **44** reduces ketones with high asymmetric inductions: 99% ee for pivalophenone, 80% ee for 2,2-dimethylcyclopentanone, and 92% ee for chloroacetophenone. The asymmetric reducing properties of this reagent closely resemble those of potassium borohydride-**43**. Asymmetric reductions of α -keto acetals have been achieved with this reagent with enantioselectivities up to > 99% ee (Eq. 43). (78)



(43)

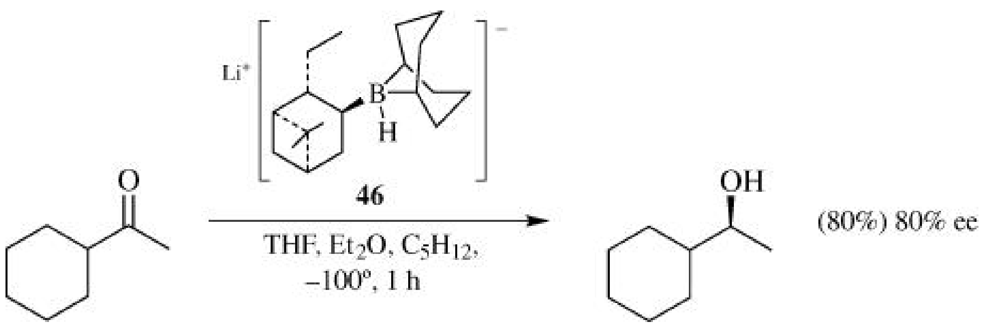
2.2.5. Chiral Alkylborohydrides

Although diisopinocampheylborane and isopinocampheylborane are excellent hydroborating agents for prochiral olefins, these reagents reduce ketones with low enantioselectivities. The reactions of lithium, sodium, and potassium hydrides with enantiopure alkylboranes forms the corresponding chiral alkylborohydrides. (79) Lithium *B*-3-pinanyl-9-borabicyclo[3.3.1]nonyl hydride (**45**) (Alpine-Hydride®) was the first enantiopure alkylborohydride that reduced ketones with moderate enantioselectivity (Eq. 44). (80)



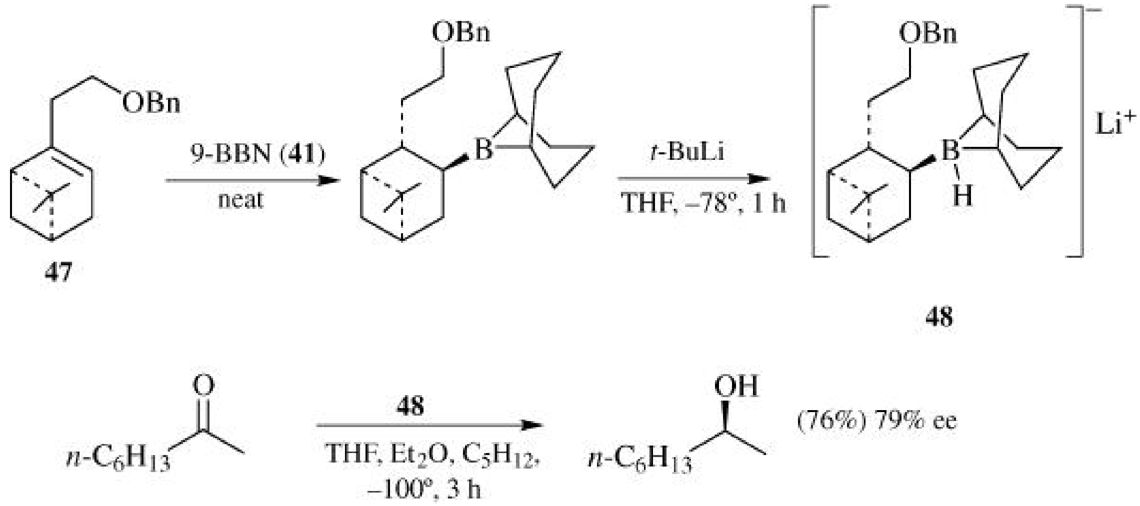
(44)

Considerable improvement is realized in the reduction of simple aliphatic ketones by the use of lithium *B*-(iso-2-ethylapopinocampheyl)-9-borabicyclo[3.3.1]nonyl hydride (**46**) (Eapine-Hydride®). Reduction of acetylcyclohexane with **46** at –100° provides the *S* alcohol in 80% yield with 80% ee (Eq. 45). (81)



(45)

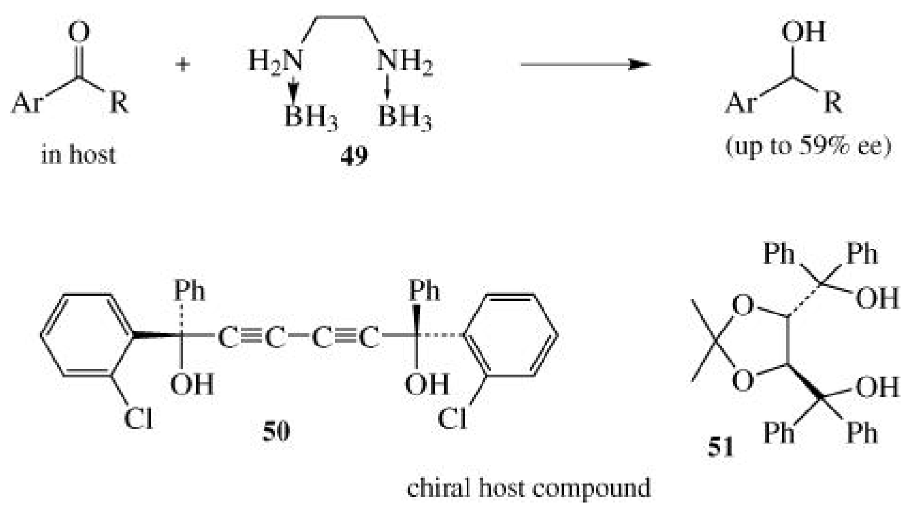
Another chiral alkylborohydride is derived from (1*R*)-(–)-nopol benzyl ether (**47**). Hydroboration of nopol benzyl ether with 9-BBN followed by treatment with *t*-BuLi gives the chiral reducing agent **48** (NB-Enantride®). (82) Although NB-Enantride reduction of relatively bulky ketones such as 3,3-dimethyl-2-butanone results in low enantioselectivity, its high efficiency in the reduction of straight-chain aliphatic ketones is noteworthy (Eq. 46). (82)



(46)

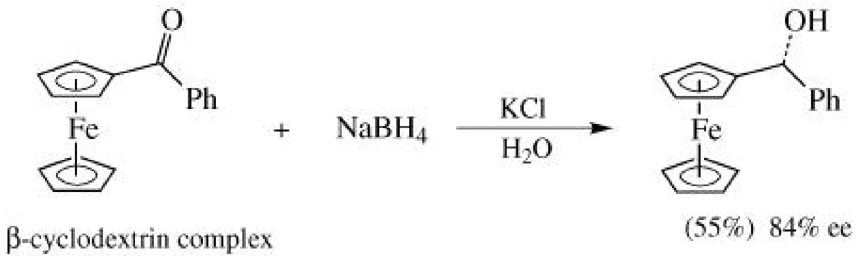
2.2.6. Ketones in Chiral Host Compounds

Treatment of solid state inclusion compounds of ketones and enantiopure host molecules such as enantiopure diols **50** and **51** with a BH_3-ethylenediamine complex **49** gives enantioenriched alcohols. (83) In this system, enantioselective reductions are achieved by the solid-solid reaction of ketones in inclusion compounds and **49**, and the enantioenriched alcohol is obtained in up to 59% ee (Eq. 47). A similar chiral environment is provided



(47)

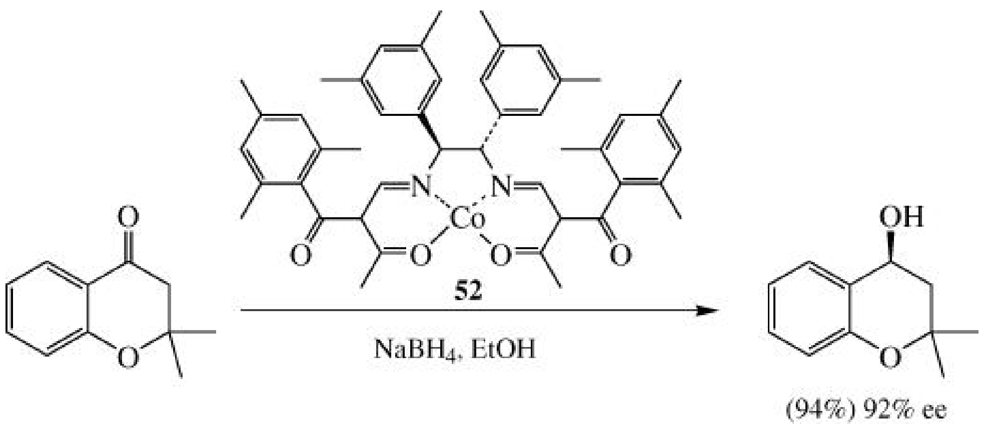
by inclusion in cyclodextrins. (84) Reduction of a ferrocenyl ketone using the aqueous suspension of β -cyclodextrin complex with $NaBH_4$ affords the enantioenriched ferrocenyl alcohol in 84% ee (Eq. 48). (85)



(48)

2.2.7. Catalytic Borohydride Reductions

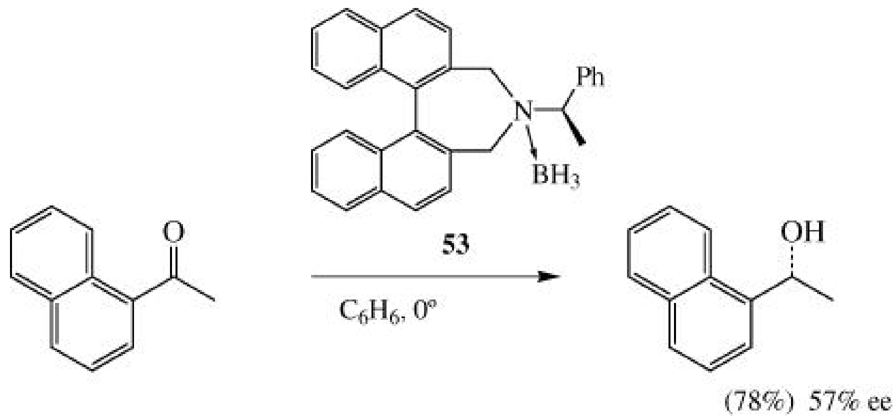
Enantioselective catalytic borohydride reduction of ketones is achieved by using an enantiopure (β -oxoaldiminato)-cobalt (II) complex as catalyst. (86) 2,2-Dimethyl-4-chromanone is reduced by $NaBH_4$ to afford the corresponding enantioenriched alcohol with 92% ee in the presence of a catalytic amount of cobalt (II) complex **52** (Eq. 49).



(49)

2.2.8. Chirally Modified Boranes

Lewis acidic boranes are suitable for modification with enantiopure bases such as amines; the resultant borane-amine complexes are used for the asymmetric reduction of ketones. (87-89) The (–)-isomer of the enantiopure amine-borane complex **53**, which is derived from (*R*)-(+)- α -methylbenzylamine and the racemic 2,2′-bis(bromomethyl)-1,1′-binaphthyl followed by separation of diastereomers, furnishes alcohols in moderate ee (Eq. 50). (90) Borane complexes **54** are also efficient reducing agents for ketones. (91) Reduction of *tert*-butyl methyl ketone with **54** gives the alcohol in 82% ee (Eq. 51).



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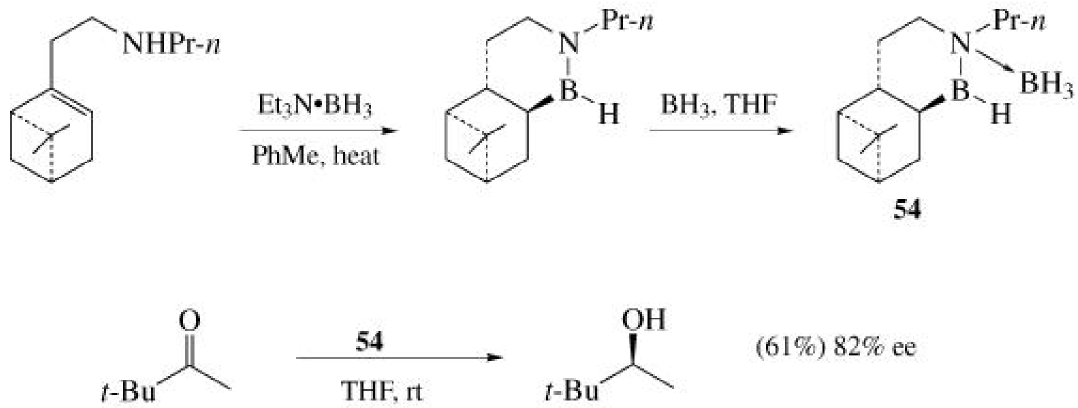
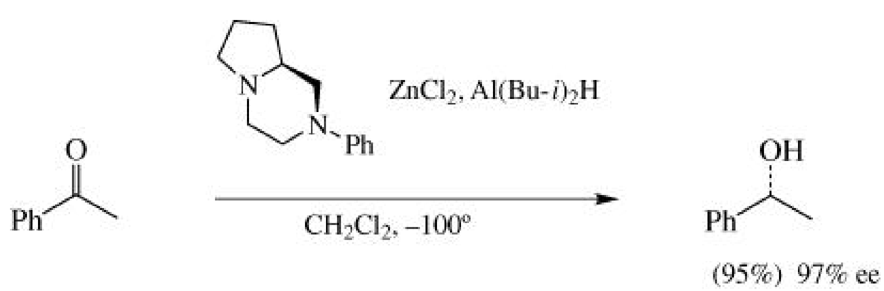


(51)

2.2.9. Chiral Diamine-Metal Hydride Systems

Chiral reducing agents prepared from tin(II) chloride, diisobutylaluminum hydride, and enantiopure diamines as ligands have been used in the reduction of prochiral ketones. (92-95) Similar reducing agents are prepared from zinc or magnesium chlorides, enantiopure diamines, and diisobutylaluminum hydride. These latter reagents reduce aromatic ketones in dichloromethane at –100° to give secondary alcohols in up to 97% ee (Eq. 52). (96)



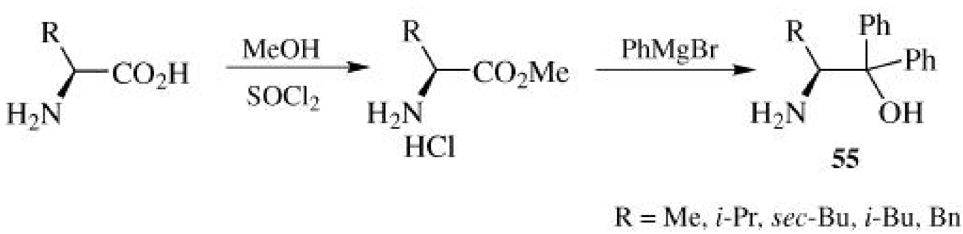
(52)

2.3. Catalytic Borane Reductions

The first effective enantioselective borane reduction of aromatic ketones utilizing stoichiometric amounts of enantiopure 1,3,2-oxazaborolidines prepared in situ from β -amino alcohols and borane was reported in 1981. (97, 98) Enantioselectivities up to 73% ee were reached with aromatic ketones, while insignificant selectivities were obtained with aliphatic ketones. Improved results were obtained by using more bulky derivatives of enantiopure α -amino alcohols derived from α -amino acids. (99) The catalytic properties of the oxazaborolidine derived from an amino alcohol and borane in the borane reduction of various functional groups were disclosed in 1985. (99, 100) A simple amino alcohol, 2-aminoethanol, dramatically increases the rate of borane reduction of ketones and aldehydes. This finding has been applied to the asymmetric version of borane reduction by using enantiopure amino alcohols. (99, 101) The catalytic behavior of chiral oxazaborolidines was first reported in the reduction of oxime ethers using a catalytic amount of an (*S*)-valine derivative in the presence of a stoichiometric amount of borane. (102) In the last ten years, oxazaborolidine chemistry has become a powerful tool for enantioselective reduction of prochiral ketones. Recently, several chiral catalyst systems other than oxazaborolidines have been developed for borane reduction of ketones. (103-108)

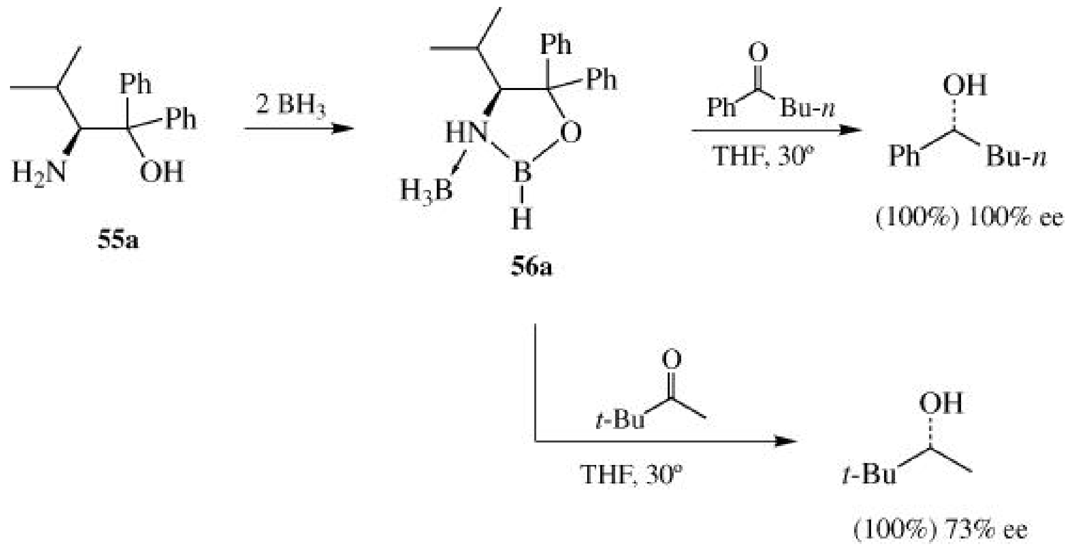
2.3.1. Chiral Oxazaborolidine Catalyzed Reductions

The first successful results in enantioselective borane reduction were obtained from enantiopure α -amino alcohols derived from L-valine derivatives. As shown in Eq. 53, α , α -diphenyl- β -amino



(53)

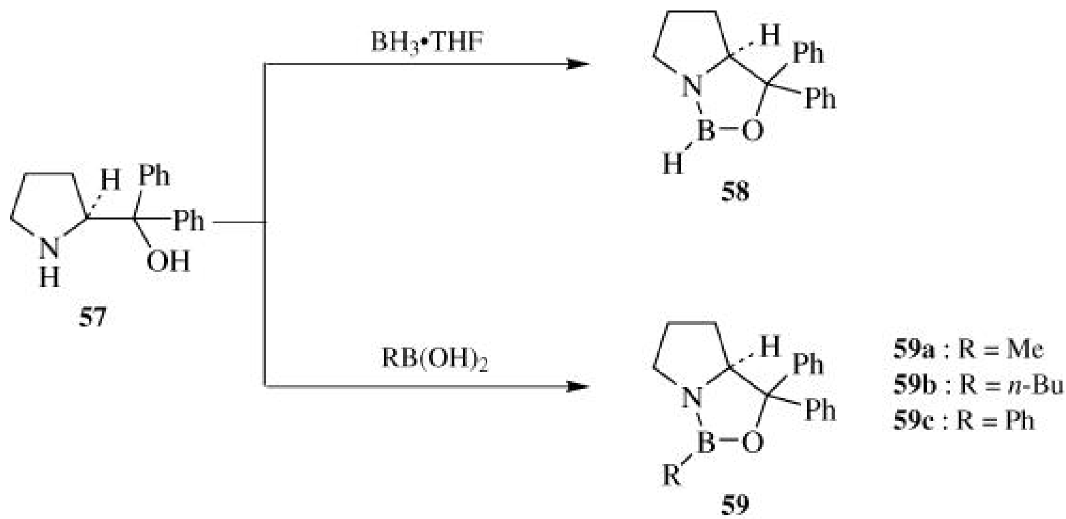
alcohols **55** are easily prepared from α -amino acids. (100) The enantioselective borane reduction of simple aromatic ketones with the oxazaborolidine **56a**, prepared in situ from borane and **55a**, gives the corresponding secondary alcohols in quantitative yield with 94–100% ee (Eq. 54). Enantioenriched



(54)

halohydrins are also obtained with high enantioselectivities by the asymmetric reduction of α -halo ketones, and can be converted into enantioenriched epoxides. Ketones with a hydroxy group protected as the trimethylsilyl ether are reduced with high enantioselectivity to give enantioenriched diols after deprotection. The reduction of methyl benzoylformate results in low selectivity (25% ee). The same reduction applied to oximes gives the corresponding enantioenriched primary amines in high chemical and enantioselectivities.

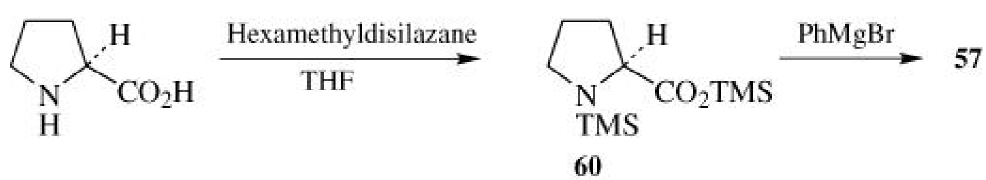
The structurally more rigid (*S*)-proline-based amino alcohol was introduced early in the study of borane reductions. (97) Sterically more hindered oxazaborolidines **58** and **59** based on (*S*)-(–)-diphenylhydroxymethylpyrrolidine **57** have been prepared and identified as efficient catalysts in borane reductions. (109-111) Oxazaborolidine **58** is prepared by reaction of α -amino alcohol **57** with excess borane followed by removal of solvent and borane under reduced pressure (Eq. 55). The *B*-alkylated borolidines **59**, which are stable and can be stored at



(55)

room temperature, are prepared from **57** and alkyl or arylboronic acids under dehydrating conditions (Eq. 55). (110, 112-114) Improved methods for making highly pure oxazaborolidines were devised by using trialkylboroxine instead of an alkylboronic acid. (115) The use of more reactive alkylboronic acid equivalents, the bis(perfluoroethyl)alkyl boronates $RB(OCF_2CF_3)_2$, permits in situ formation of the oxazaborolidines, which show comparable results in the asymmetric reduction of ketones. (116)

Amino alcohol **57** is prepared from (*S*)-proline by several methods. The Grignard reaction of L-proline trimethylsilyl ester **60** (Eq. 56), (117) the alkyl esters, (118) the ester hydrochlorides, (119) (*S*)-proline-*N*-carboxyanhydride (**61**) (Eq. 57), (115)



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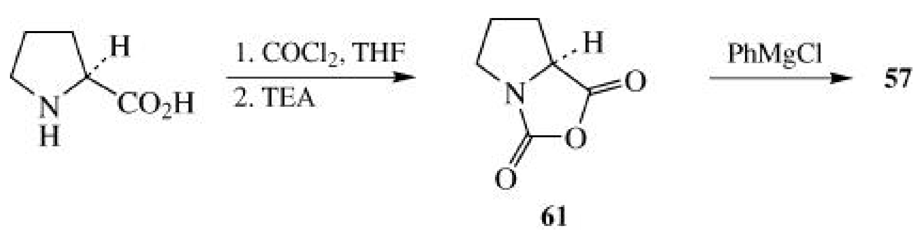
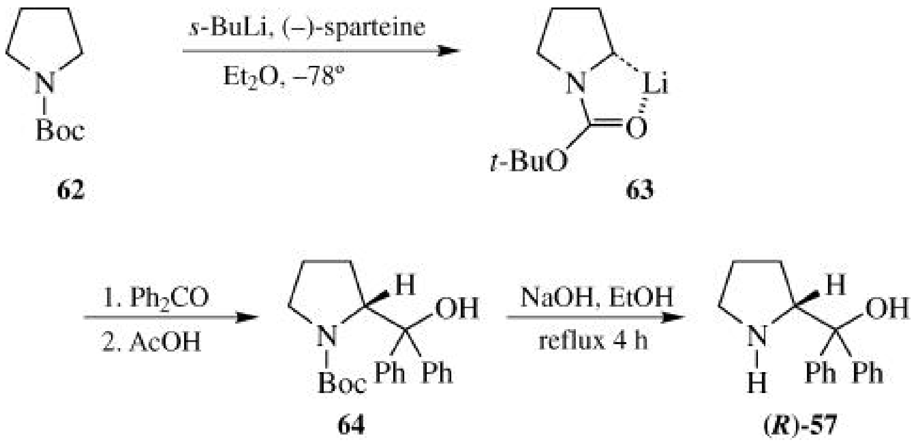


(57)

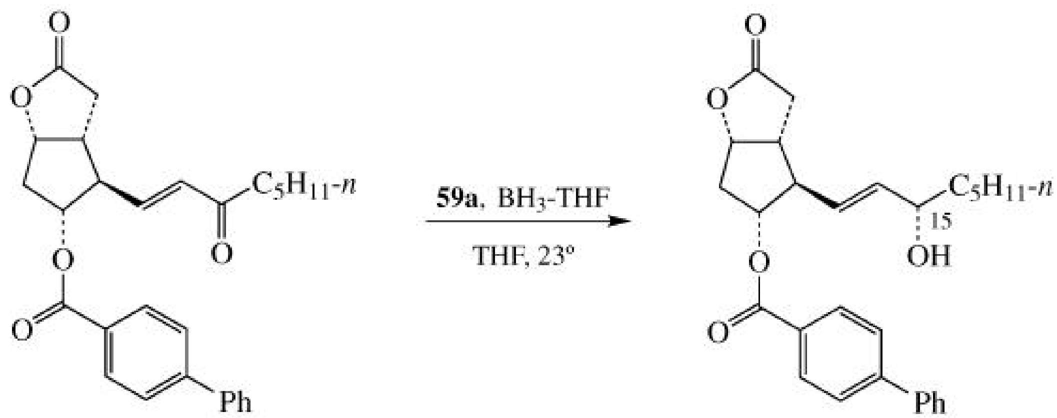
N-benzyloxycarbonyl-(*S*)-proline esters, (109, 111, 118) or the corresponding *N*-benzyl derivatives (120) with phenylmagnesium halides lead to (*S*)-**57**. The preferred method for obtaining the *R* catalyst is based on enantioselective deprotonation of Bocpyrrolidine (**62**) with *sec*-BuLi in the presence of (–)-sparteine. (121) The chiral organolithium intermediate **63** undergoes reaction with benzophenone to give (*R*)-**64** in 70% yield and 99.3% ee after one crystallization. Removal of the Boc group with sodium hydroxide gives (*R*)-**57** in 90% yield (Eq. 58). An alternative



(58)

route to (*S*)- and (*R*)-**57** is the use of racemic pyroglutamic acid followed by resolution. (109)

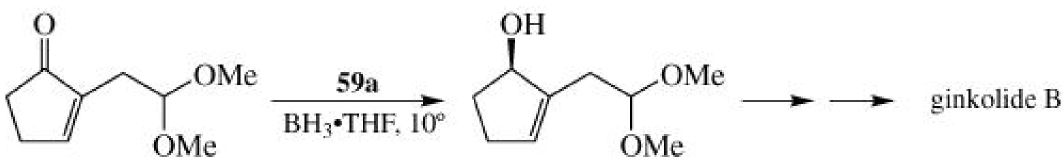
In the presence of catalyst **58**, various ketones are reduced asymmetrically with high enantioselectivity. For example, borane reduction of acetophenone in the presence of 10 mol % of **58** at 25° affords (*R*)-1-phenylethanol in 100% conversion with 97% ee. Catalysts (*S*)-**58** and (*S*)-**59** have been tested in the reduction of several ketones. The corresponding alcohols of *R* configuration are obtained with excellent enantioselectivities. Oxazaborolidine-catalyzed reductions have been used as a key step in the synthesis of various natural products. For example, catalytic reduction using **59a** has been used in prostaglandin synthesis. (110) The enantiopure oxolactone shown in Eq. 59 is reduced to a 90:10 mixture



(59)

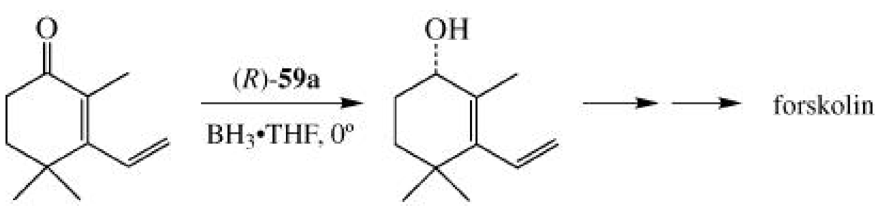
65 (90%) de = 90:10

of diastereomers in which (15*S*)-**65** predominates. Several other therapeutically important compounds such as ginkolide B (Eq. 60), (122) forskolin (Eq. 61), (123) and Fluoxetine® (Eq. 62) (124) have been synthesized using a catalytic borane reduction



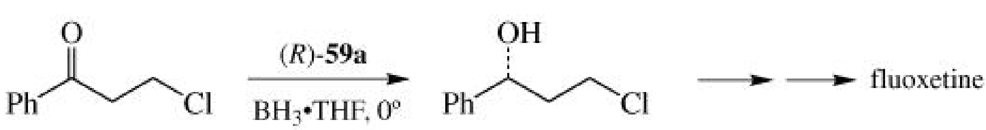
(60)

(88%) 93% ee



(61)

(85%) 90% ee

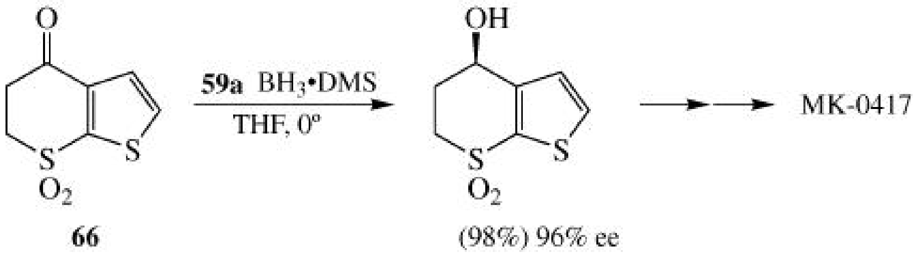


(62)

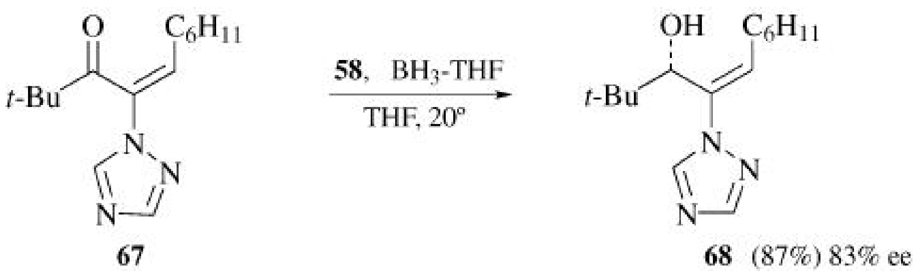
(99%) 94% ee

as the key step. The synthesis of enantiomerically pure MK-0417 involves the asymmetric borane reduction of sulfone **66** (Eq. 63). (125) Reduction of

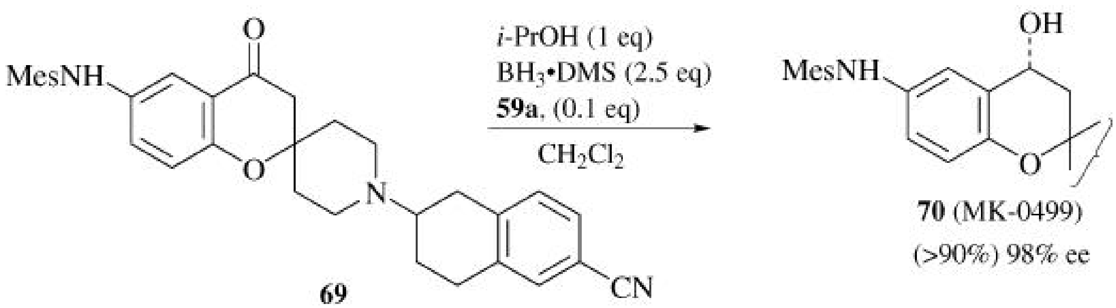
(*E*)-enone **67** gave the plant growth regulator triapentenol ((*S*)-**68**) (Eq. 64). (118) The antiarrhythmic drug candidate MK-0499 (**70**) was also prepared by reduction of the corresponding ketone **69** (Eq. 65). (126) In this report the enantioselectivities in the catalytic reduction of the ketone were enhanced by addition of achiral alcohols such as 2-propanol or amines such as triethylamine (Eq. 66). The oxazaborolidine catalyst **59c** is effective for the reduction of acyldithianes. (114)



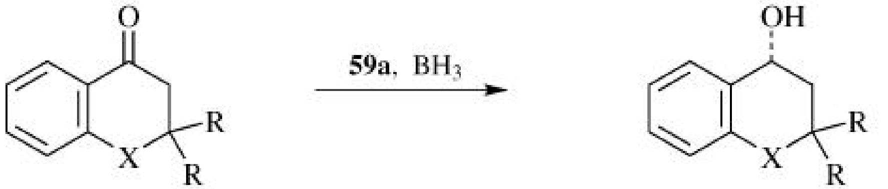
(63)



(64)



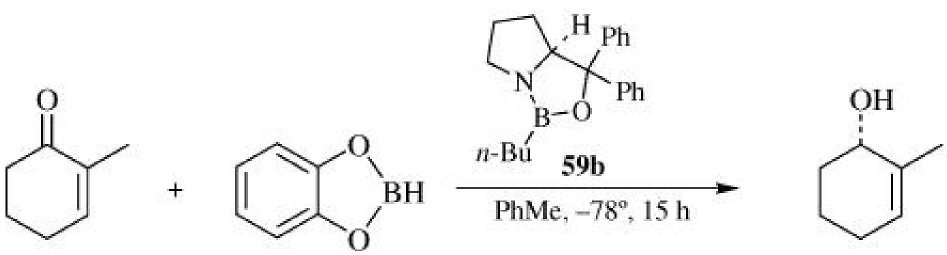
(65)



R	X	% ee without *i*-PrOH	% ee with *i*-PrOH
H	CH_2	90	98
H	O	93	98
Me	O	93	99
$(CH_2)_5$	O	91	99

(66)

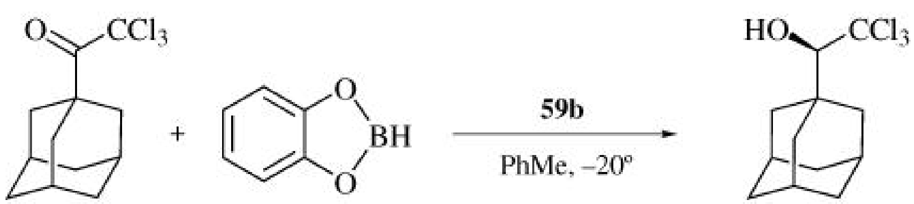
Catecholborane (1,3,2-benzodioxaborole) (**71**) can be used instead of borane as a reductant. The advantage of catecholborane is that the uncatalyzed reaction is suppressed. Enantioenriched allylic alcohols can be obtained by catalytic reduction of enones with catecholborane (Eq. 67). (113) Some trichloromethyl and trifluoromethyl ketones are reduced with catecholborane in the presence of **59b** (Eq. 68). Further reactions on the enantioenriched trichloromethyl carbinol **72**



71

(>95%) 93% ee

(67)

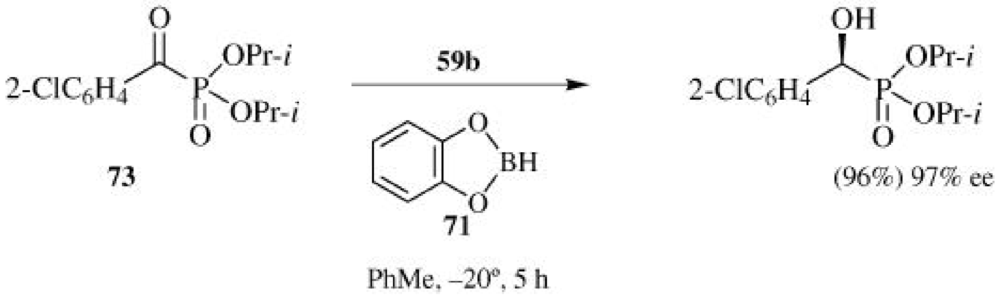


71

72 98% ee

(68)

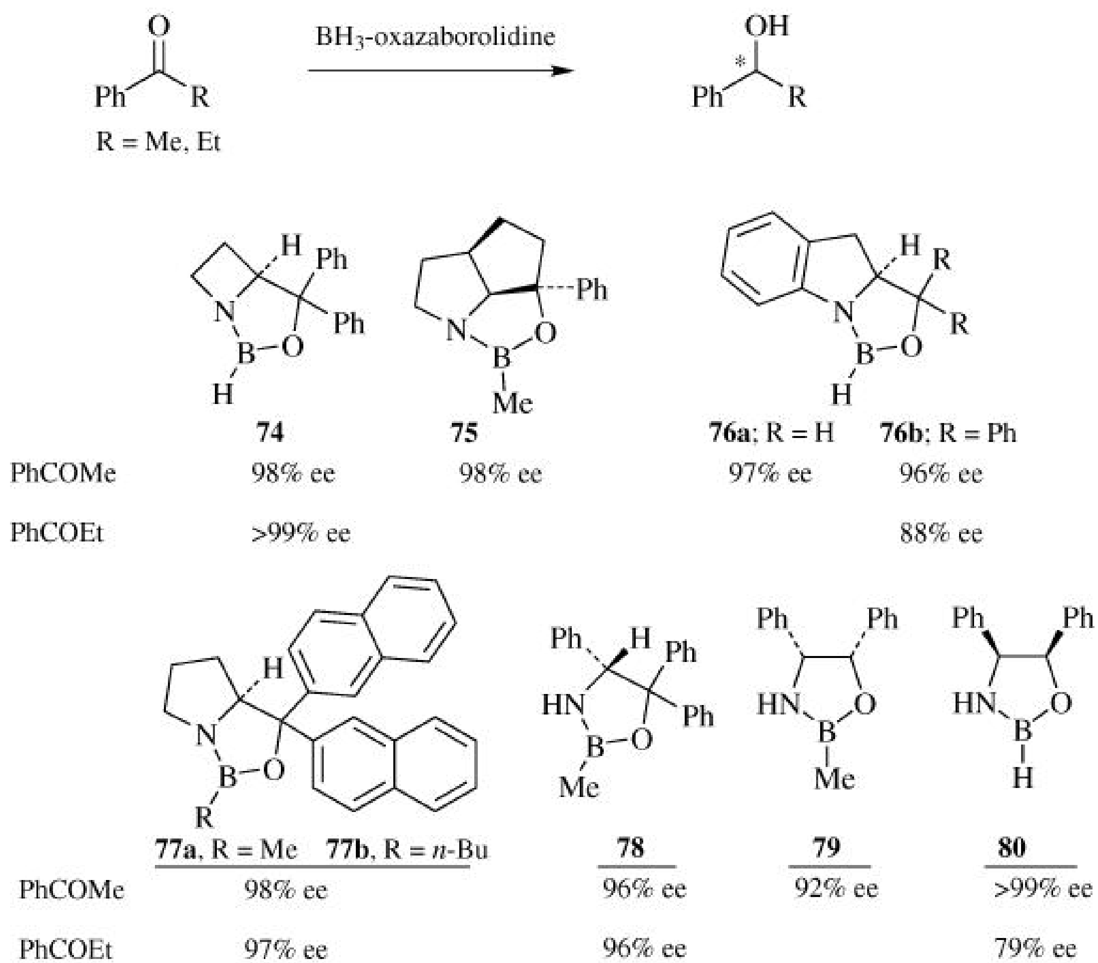
lead to enantioenriched α -hydroxy acids (127) or α -amino acids. (128) A highly enantioselective reduction of keto phosphonates such as **73** with catecholborane is achieved with oxazaborolidine catalyst **59b**. (129) The reaction gives good chemical yields and excellent enantiomeric excesses (Eq. 69). Deuterated catecholborane



(69)

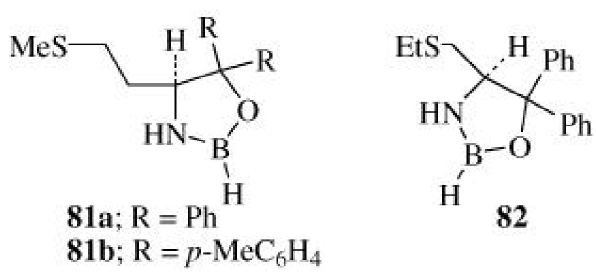
has been used for the asymmetric reduction of aldehydes. (112) Enantioenriched 1-deuterio primary alcohols are obtained by reduction at –126° for 3.5 hours with excellent enantioselectivities.

Enantiopure oxazaborolidines other than **56**, **58**, and **59** have been tested as catalysts in the asymmetric borane reduction of ketones. Acetophenone and propiophenone have been employed as the model substrates in many cases (Eq. 70).

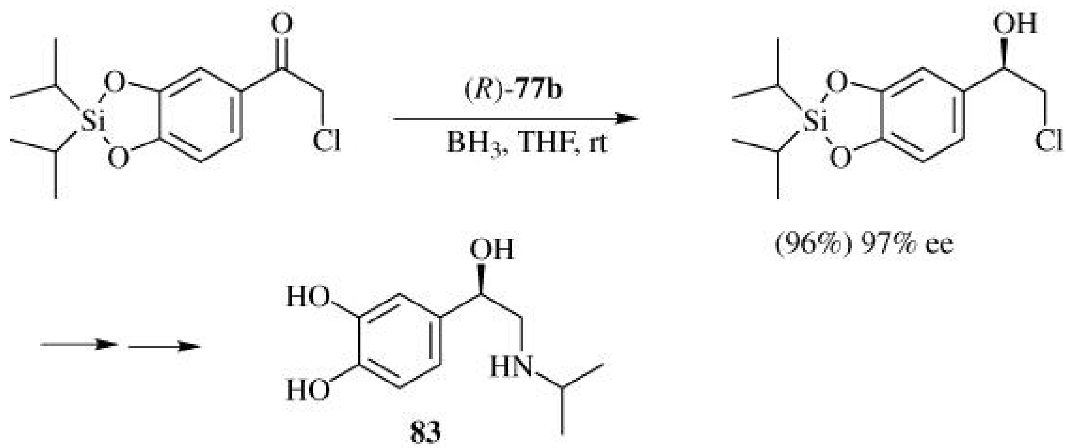


(70)

High enantioselectivities in the reduction of ketones were obtained with oxazaborolidines **74-80** as catalysts. The β -naphthyl catalysts **77** are in several instances more effective than the phenyl analogs. The catalyst (*R*)-**77b** (R = *n*-Bu) has been used in the synthesis of isoproterenol (**83**), a β -adrenoreceptor agonist

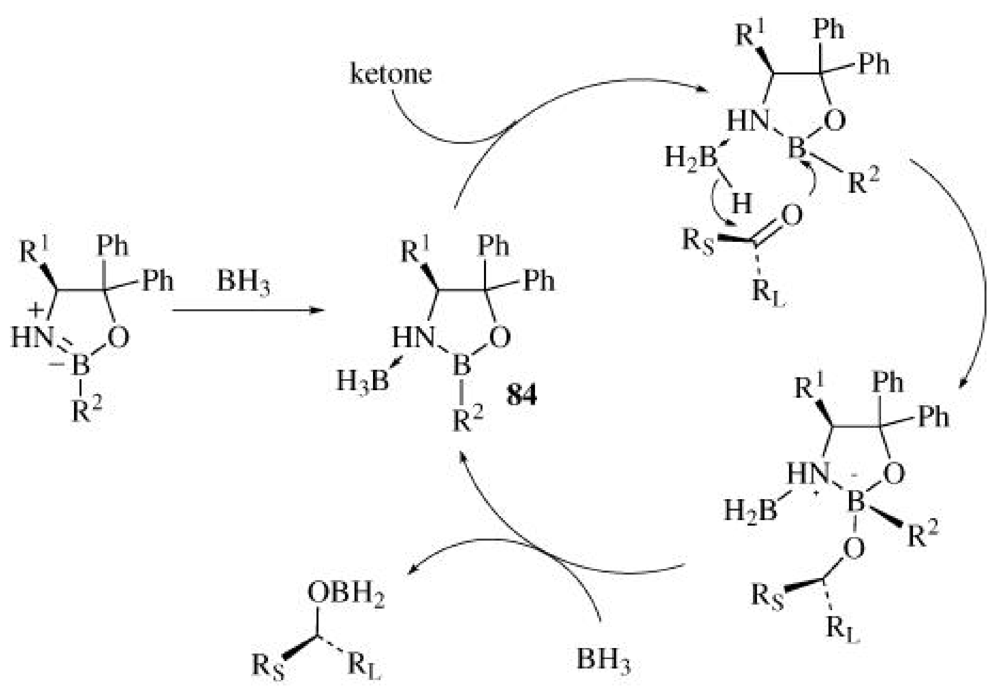


(Eq. 71). (132) The catalysts containing thioether groups, **81** and **82**, gave excellent selectivities in the reduction of α -halo ketones. The reduction of *w*-bromoacetophenone with the catalyst **81** or **82** gives the corresponding alcohol in high chemical yield with 100% ee. (130, 131)



(71)

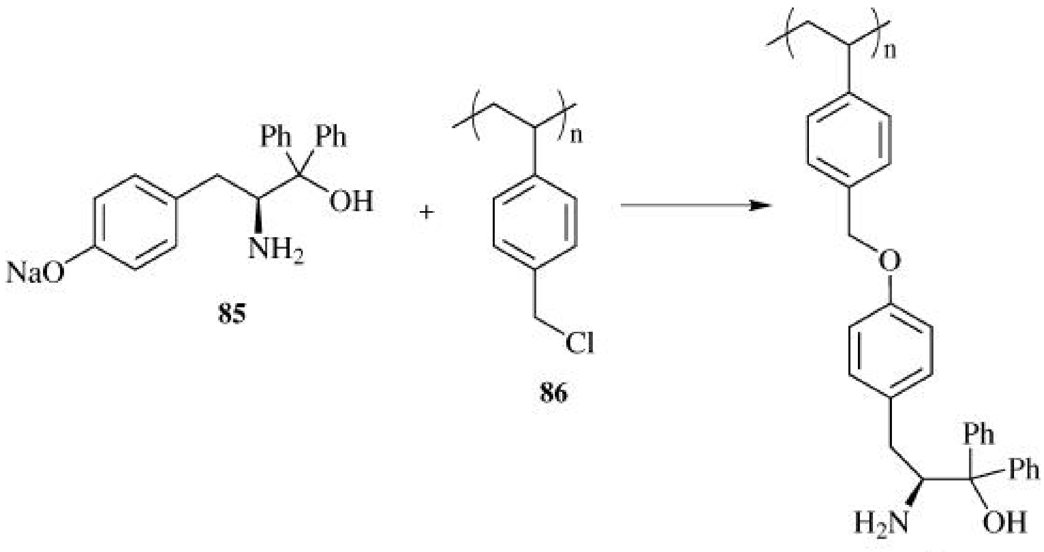
The mechanism of chiral oxazaborolidine-catalyzed ketone reduction has been suggested to involve the formation of borane adduct **84**. The borane coordinated to the oxazaborolidine nitrogen increases the acidity of the ring boron, facilitating coordination of the ketone to be reduced. A possible mechanism involving a six-membered transition state is given in Eq. 72. Mechanistic details



(72)

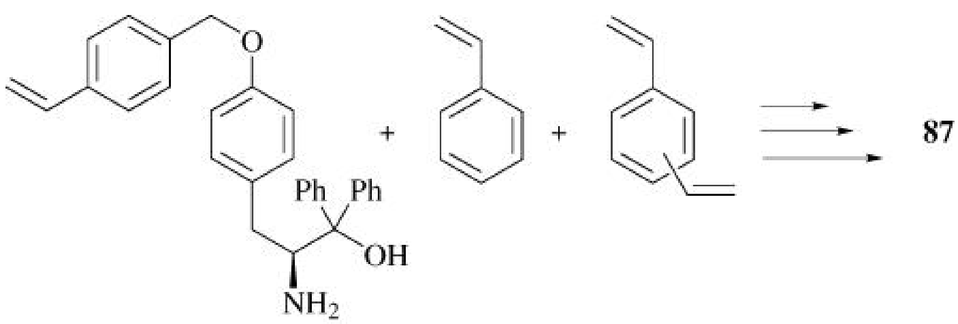
of the catalysis have been also investigated using *ab initio* molecular orbital calculations. (133-135)

Polymer-supported oxazaborolidine catalysts have also been used. Enantiopure α -amino alcohol **85** is attached to the partially chloromethylated crosslinked polystyrene **86** through a benzyl ether linkage. A polymer-supported chiral α -amino alcohol **87** is obtained easily by this method (Eq. 73). (101, 136) An alternative route to the polymer-supported amino alcohol is polymerization of monomer **88** with styrene, using divinylbenzene as a crosslinking agent (Eq. 74). (137)



87

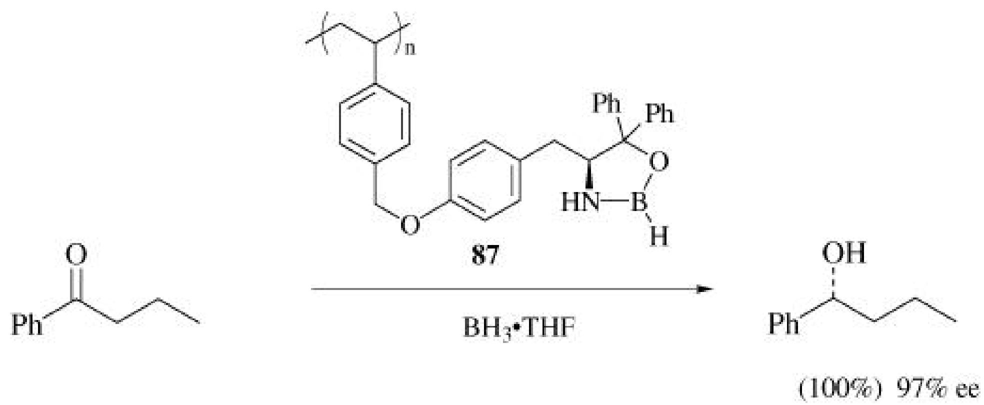
(73)



88

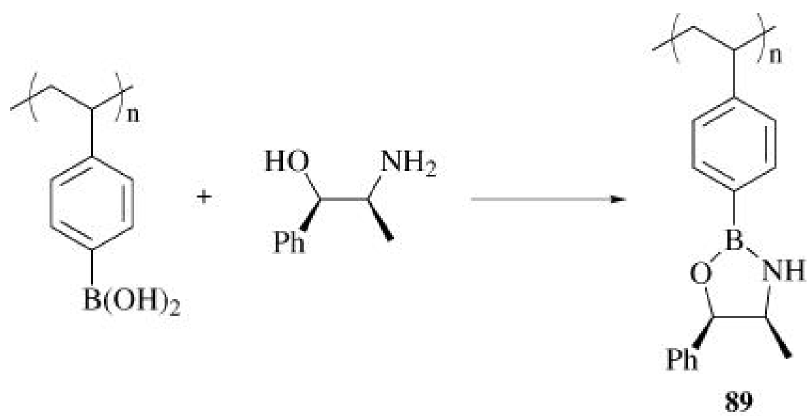
(74)

Borane reduction of butyrophenone using the polymeric catalyst **87** gives the alcohol in quantitative yield with 97% ee (Eq. 75). (101) The polymeric catalysts can be separated



(75)

easily from the reaction mixture by simple filtration and reused several times. One of the more attractive ways of performing the asymmetric synthesis with an insoluble polymeric catalyst is using a flow system, in which the prochiral substrate is converted into the enantioenriched product by passing through a column filled with the polymeric catalyst. Such a system was developed for the asymmetric reduction of ketones using the polymeric catalyst **87**. (136) Other polymer-supported oxazaborolidine catalysts such as **89** (Eq. 76) have also been used for ketone reductions (Eq. 77). (138, 139)

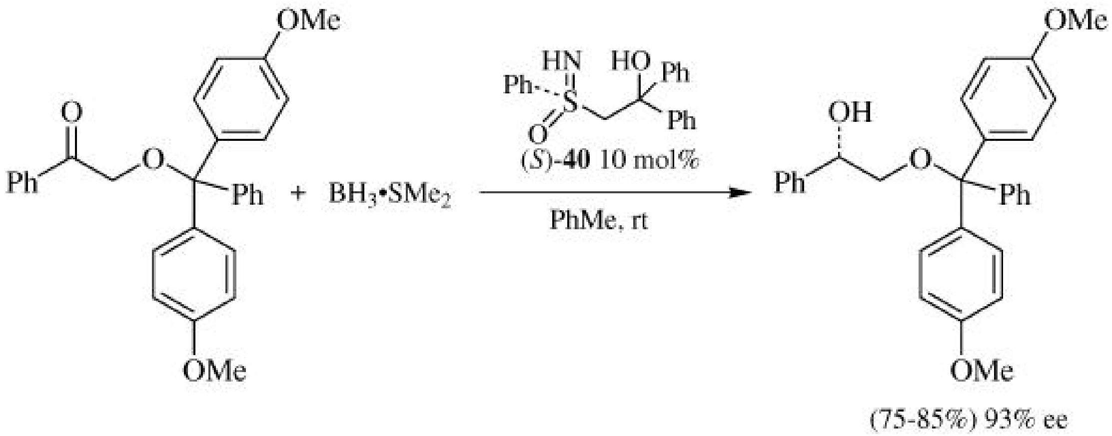


(76)

(77)

2.3.2. Other Catalysts for Borane Reductions

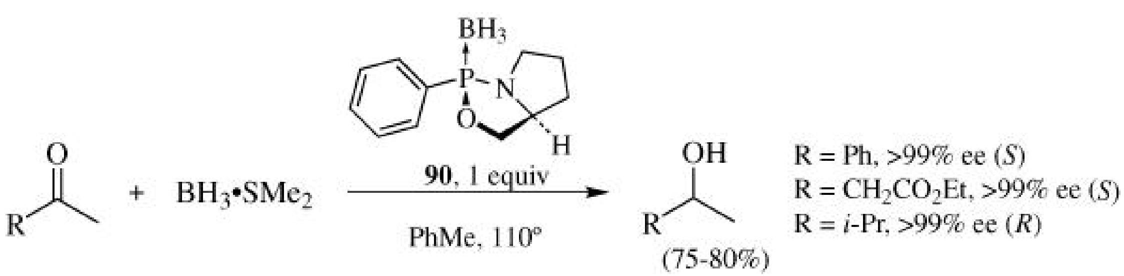
Enantiopure β -hydroxysulfoximines **40** catalyze the enantioselective borane reduction of ketones affording secondary alcohols in high yields with good enantioselectivities (Eq. 78). (140) Protected



(78)

α -hydroxy ketones and α -halo ketones give the best results, affording the reduced products in up to 93 and 84% ee, respectively. Enantiopure β -hydroxy sulfoximine **40** also catalyzes asymmetric reduction with the $NaBH_4$-Me_3SiCl mixed reagent instead of borane. (73)

Another example of asymmetric reduction catalysts not based on the oxazaborolidine structure is the oxazaphospholidine-borane complex. Enantiopure oxazaphospholidine-borane **90** promotes asymmetric reduction of ketones with borane. (108) Although the mechanistic features have not been investigated, both aromatic and aliphatic ketones are reduced with borane in the presence of 1 equivalent of **90** at 110° in toluene to give alcohols with high enantioselectivity (Eq. 79). A similar compound, the dihydrobenzazaphosphole-borane complex,

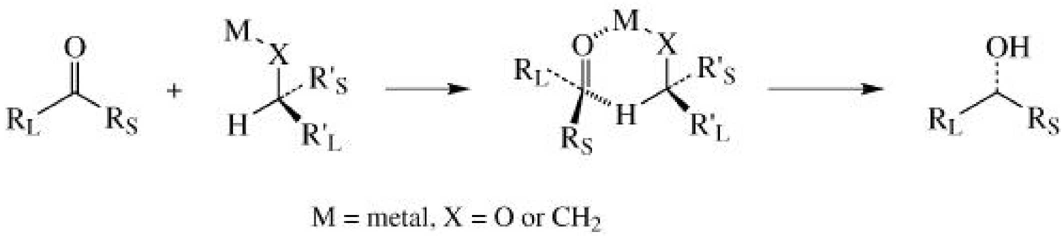


(79)

shows catalytic activity in the borane reduction of ketones. (107) Enantiopure phosphinamides are also used as catalysts in the borane reduction. However, enantioselectivities obtained with these catalysts are only moderate. (106, 141)

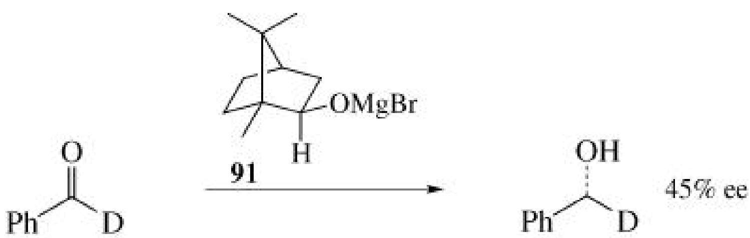
2.4. Meerwein-Ponndorf-Verley Reductions

Asymmetric reductions with transfer of the β hydrogen of metal alkoxides or metal alkyls to carbonyl compounds have been studied extensively. Various metals including aluminum, magnesium, zinc, potassium, and boron have been used as counterions in this type of reducing agent. Enantioselective Meerwein-Ponndorf-Verley (MPV) reductions of ketones are suggested to proceed by a six-membered transition state to give enantioenriched alcohols (Eq. 80).



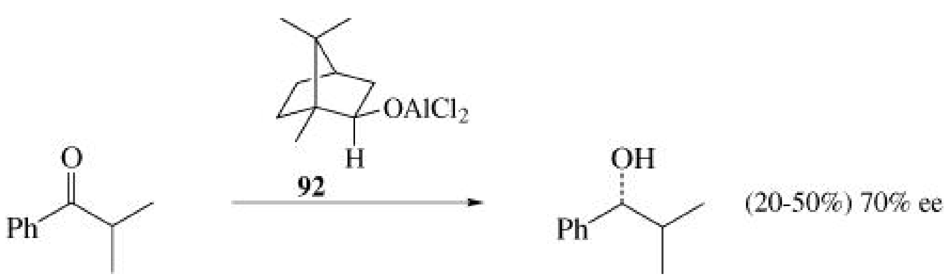
(80)

The magnesium alkoxide of (–)-isoborneol (**91**) has been used for the reduction of benzaldehyde-*d*. The hydride of **91** is transferred asymmetrically to benzaldehyde-*d* to give (*R*)-benzyl alcohol-1-*d* in 45% ee (Eq. 81). (142) The aluminum



(81)

analog, dichloroaluminum alkoxide of (–)-isoborneol **92**, has been used for the reduction of several ketones. Phenyl isopropyl ketone is reduced with this reagent with 70% ee (Eq. 82). (143)

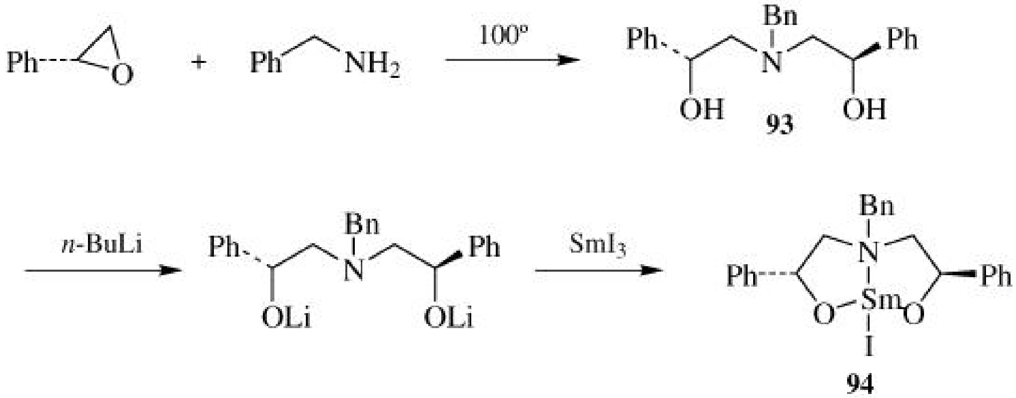


(82)

2.4.1. Asymmetric Transfer Hydrogenation

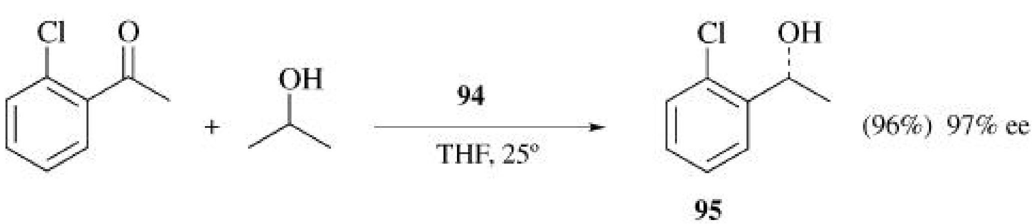
Catalytic versions of asymmetric Meerwein-Ponndorf-Verley reduction have been developed. (144) The MPV reduction of prochiral ketones is catalyzed by chirally modified transition metal ions such as Sm(III), Rh(I), Ir(I), and Ru(II). These complexes promote asymmetric reduction at high substrate/catalyst mol ratios in 2-propanol at ambient temperature to reflux. This method has been studied extensively because of the low cost and favorable properties of the hydrogen donor as well as the operational simplicity.

Chiral nitrogen-containing ligands have been used widely in asymmetric hydrogen transfer reactions. (145) A samarium(III) complex of amino diol **93** is an efficient catalyst for the enantioselective reduction of ketones. Double deprotonation of **93** with hydroxide-free *n*-BuLi and subsequent complex formation with SmI_3 in tetrahydrofuran provides the Sm complex **94** (Eq. 83). In the presence of



(83)

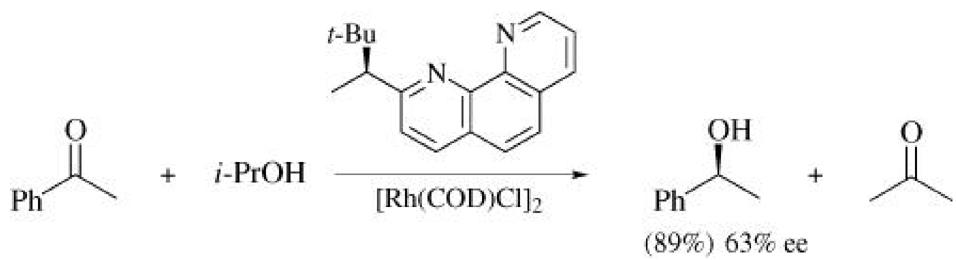
5 mol % of **94**, the reduction of *o*-chloroacetophenone by 2-propanol is achieved in 2 hours at ambient temperature to give (*R*)-alcohol **95** in 97% ee and 96% yield (Eq. 84). (146) Simple aryl methyl ketones afford enantiomeric excesses > 92% using



(84)

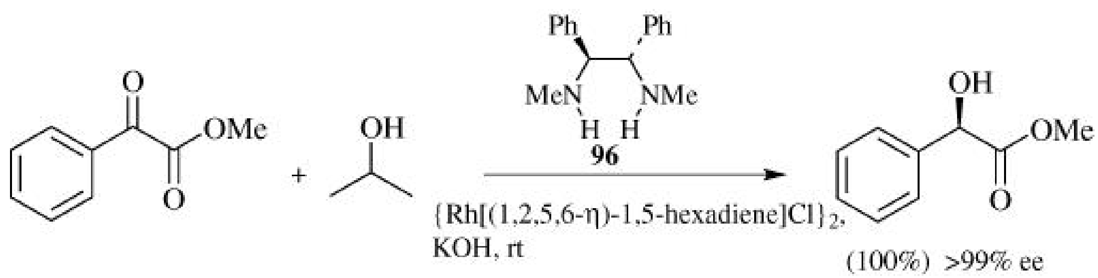
this system. Other lanthanide(III) complexes derived from YI_3, NdI_3, and TbI_3 are also active catalysts and give high enantioselectivities.

Rhodium catalysts containing enantiopure bipyridine or phenanthroline derivatives have been used in the reduction of ketones. The Rh-catalyzed reduction of acetophenone with 2-propanol is shown in Eq. 85. (147) A pentacoordinated



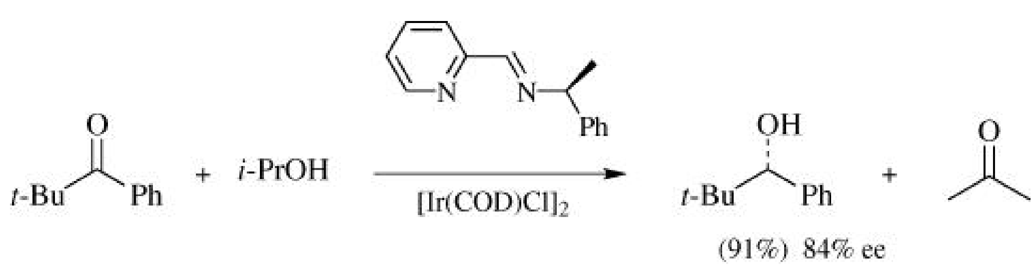
(85)

hydridorhodium complex is postulated as an intermediate in the catalytic cycle. In the presence of the Rh catalyst derived from enantiopure diamine **96**, methyl phenylpyruvate is reduced to the *R* alcohol in 100% conversion and > 99% ee (Eq. 86). (148, 149) However, acetophenone is reduced in only 67% ee. Similar results are obtained by using a silica-supported catalyst in a continuous flow reactor. (148)



(86)

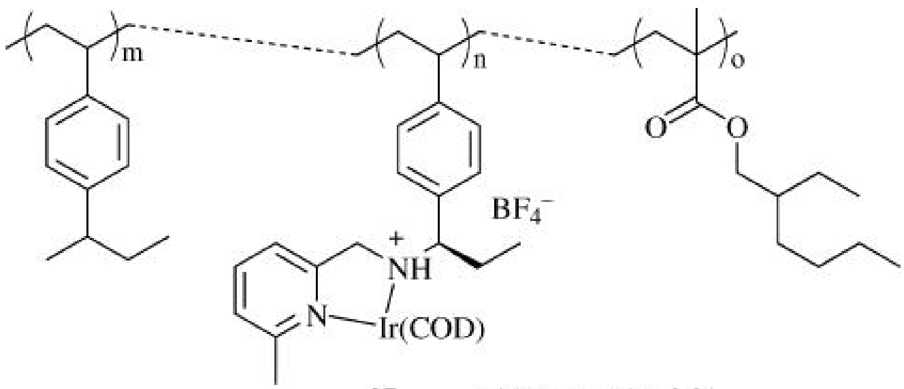
Transfer hydrogenation of simple ketones with 2-propanol catalyzed by iridium complexes containing enantiopure dinitrogen ligands has been reported. Alkylaminomethyl- and alkyliminomethylpyridines are used as ligands in the Ircatalyzed reductions. Reduction of bulky *tert*-butyl phenyl ketone with an Ir catalyst affords the corresponding alcohol in 84% ee (Eq. 87). (150) Polymer-supported



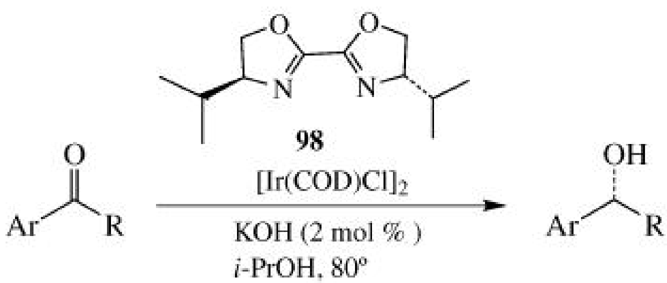
(87)

enantiopure diamine ligands have been used for the same reaction. (151) Enantioselectivities up to 86% ee are obtained by using the polymeric catalyst

97 in the reduction of simple ketones (Eq. 88). Bisoxazolines **98** having C_2 symmetry, KOH, and 2-propanol reduce aromatic ketones to the corresponding secondary alcohols with up to 91% ee (Eq. 89). (52) An iridium complex with



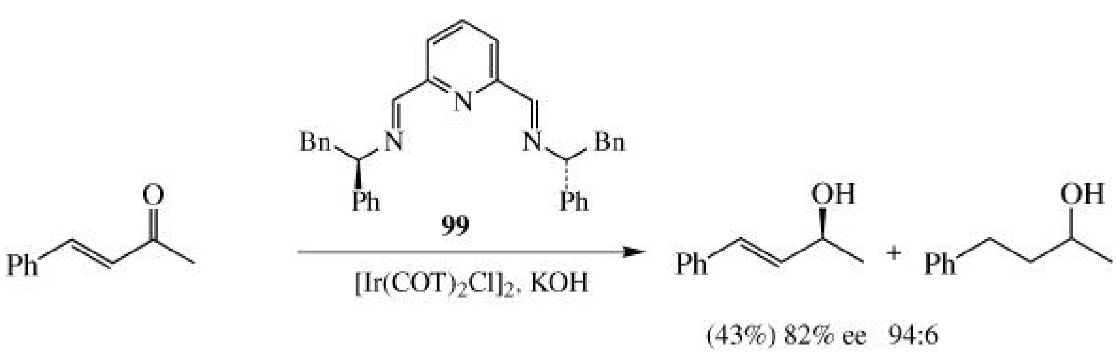
97 n / (m + n + o) = 0.01 (88)



Ar	R	%ee
Ph	Me	58
$C_{10}H_7$-2	Me	63
Ph	*i*-Pr	91

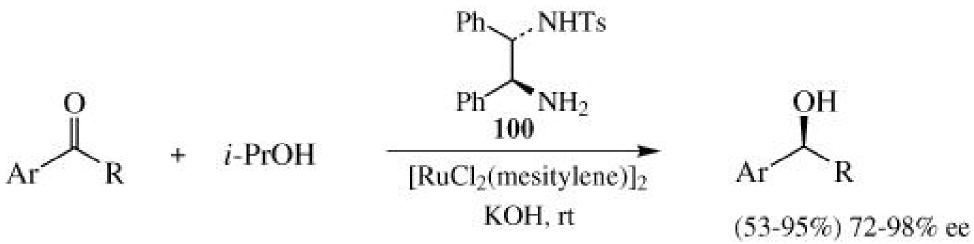
(89)

2,6-pyridine-1,2-diphenylethyldiimine (**99**) is active in transfer hydrogenation. (153) Reduction of an α , β -unsaturated ketone in this way affords the allylic alcohol in 82% ee (Eq. 90).



(90)

A new type of chiral Ru(II) catalyst **100** effects highly enantioselective reductions of aromatic ketones at room temperature (Eq. 91). This catalyst system is much more reactive than the previously reported transition metal complexes. (154) A variety of simple aromatic ketones are transformed to the corresponding secondary

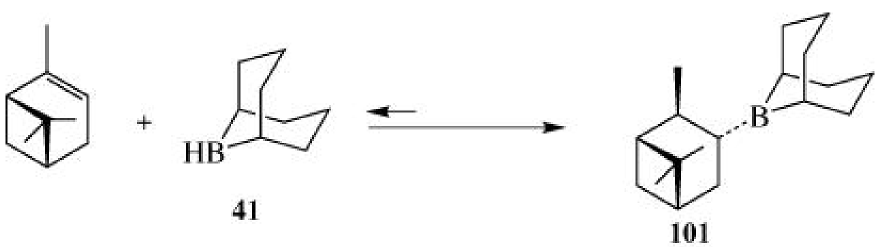


(91)

alcohols with high enantiomeric purity in high substrate/catalyst mole ratios (200–500). The reduction of acetophenone occurs in 97% ee and 95% yield.

2.4.2. Chiral Alkylboranes

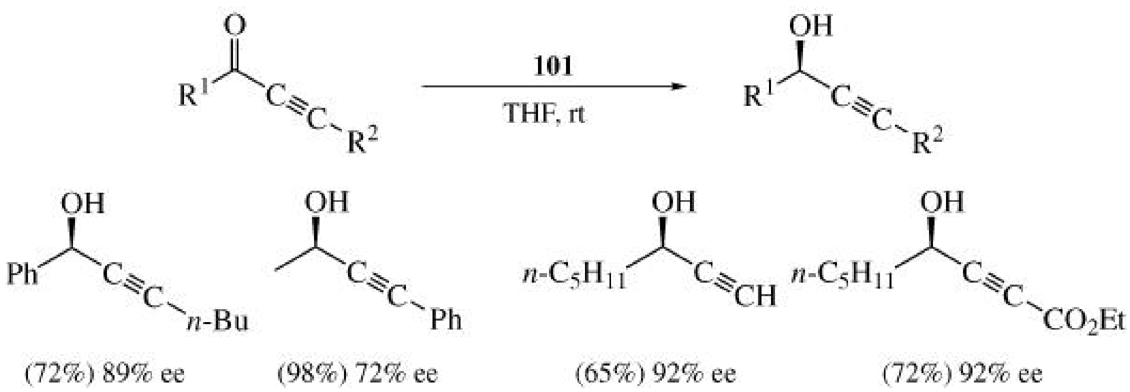
Enantiopure alkylboranes have been studied extensively as enantioselective reducing agents for various ketones. Although these reductants are not catalytic, the enantiopure alkylboranes reduce a wide variety of ketones efficiently. For example, *B*-(3-pinanyl)-9-borabicyclo[3.3.1]nonane **101** (Eq. 92), which is commercially available as Alpine-Borane®, shows excellent reducing



(92)

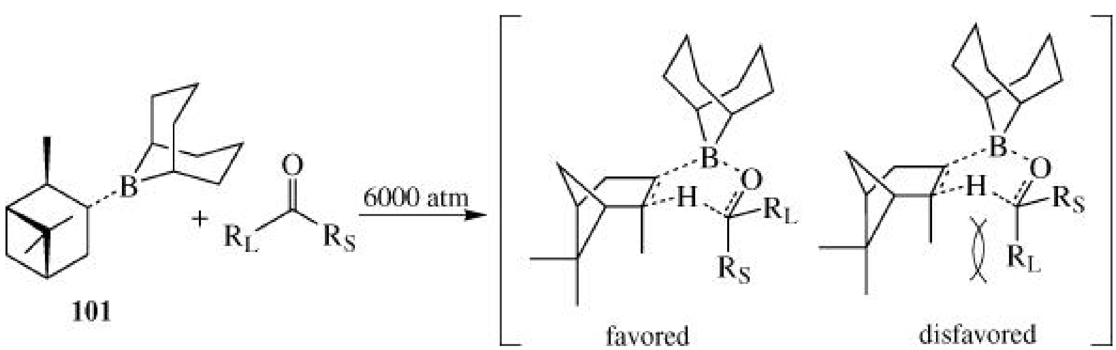
properties for certain carbonyl compounds. (155-159) The reduction of deuterated aldehydes is very fast, and the enantiopure deuterated primary alcohols are obtained in 90% ee (Eq. 93). (158) Reductions of acetylenic ketones are also fast, and the products are usually obtained in excellent ee (Eq. 94). However, the

(93)



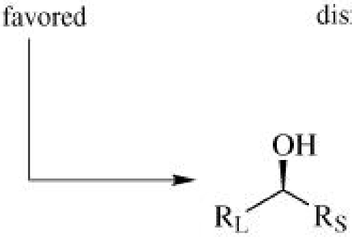
(94)

asymmetric reduction of most other ketones with this reagent is slow, and low enantioselectivities are obtained. For example, reduction of acetophenone to phenylethyl alcohol proceeds with only 10% ee. In slow reductions, a competing dissociation of the reagent into its components takes place (Eq. 92). Nonasymmetric reduction with 9-BBN results in an achiral product. The use of the neat reagent **101** enhances the reaction rate and improves enantioselectivity. Asymmetric reduction of acetophenone with neat **101** gives the *S* alcohol in 78% ee and 68% yield. (160, 161) Further improvement occurs when the reduction is performed at high pressure, since the bimolecular asymmetric reduction is accelerated while the undesired dissociation process is suppressed. At 2000–6000 atm and 25°, reductions are accelerated approximately 3- to 15-fold, respectively. Thus, acetophenone is reduced with 98% ee at 2000 atm in 3 days, and is completely reduced in less than 24 hours at 6000 atm (Eq. 95). (162)

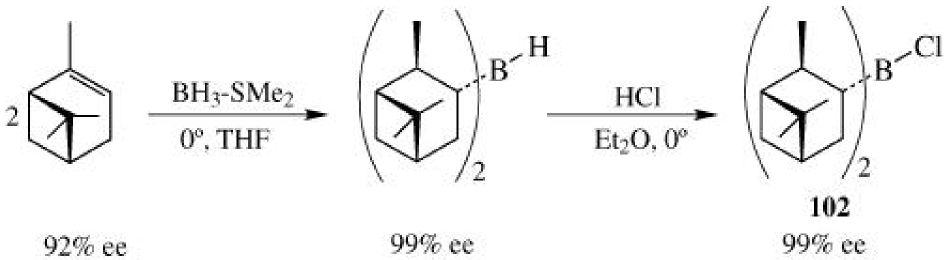


(95)

R_L	R_S	% ee	% ee (1 atm)
Ph	Me (80%)	100	78
C_5H_4N-3	Me (67%)	100	90
i-Pr	Me (90%)	90	57
n-C_6H_{13}	Me (63%)	63	44

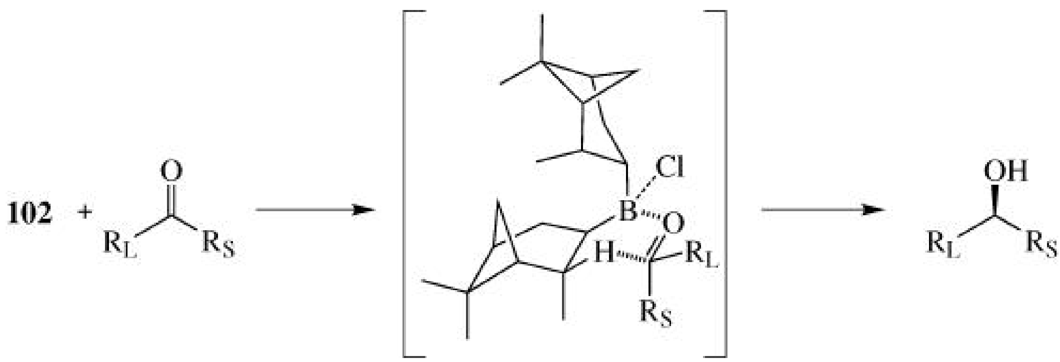


An alternative enantiopure alkyl borane reducing agent is *B*-chlorodiiso-pinocamphenylborane (**102**), which is readily prepared from α -pinene (92% ee) in high chemical and optical purities (99% ee) by hydroboration followed by treatment with dry hydrogen chloride in ether (Eq. 96). This reagent is commercially



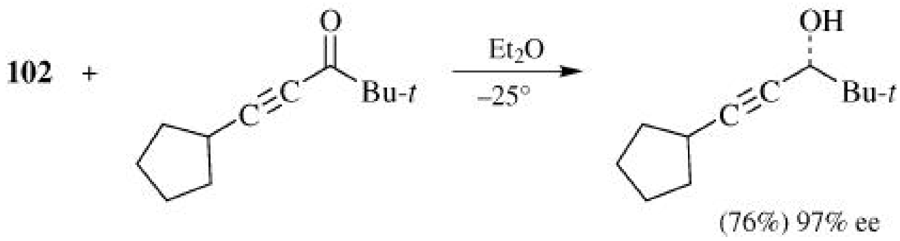
(96)

available as DIP-Chloride®. Since the reactivity of this reagent is higher than that of Alpine-Borane®, **102** is effectively used for the asymmetric reduction of a wide range of ketones (Eq. 97). (163-166) Simple aryl alkyl ketones can be reduced rapidly to afford the alcohols in high enantioselectivities. (164)



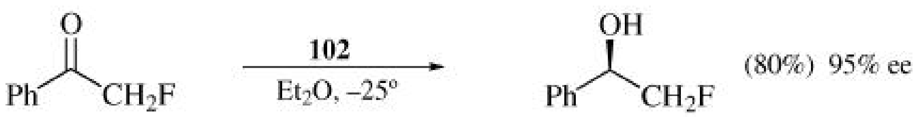
(97)

Although the reduction of straight-chain aliphatic ketones such as 2-butanone and 2-octanone shows low selectivity, α -tertiary alkyl ketones are reduced in excellent enantioselectivities. The reduction of alicyclic ketones is rapid and high ees are typically obtained. Whereas Alpine-Borane® (**101**) gives poor results with hindered acetylenic ketones, DIP-Cl **102** reduces these substrates to the propargylic alcohols in high ee (Eq. 98). Perfluoroalkyl acetylenic ketones can be



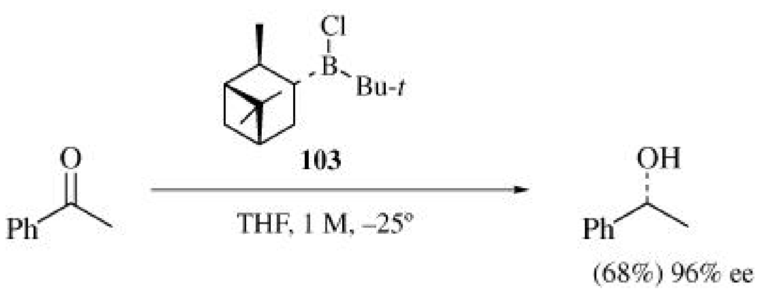
(98)

reduced with this reagent in high ee. For example, 1,1,1-trifluoro-4-phenyl-3-butyn-2-one, and 1,1,1,2,2-pentafluoro-5-phenyl-4-pentyn-3-one are reduced with **102** in ether at –25° within 0.5–2 hours in 98% and 96% ee, respectively. (167) Reduction of trifluoromethyl ketones also proceeds with high enantiomeric induction. (168) The sense of asymmetric induction in the enantioselective reduction of aryl trifluoroalkyl ketones differs from that of the corresponding mono and difluoromethyl ketones. (169) While 2-fluoroacetophenone is reduced to the *R* alcohol in 95% ee (Eq. 99), the reduction of trifluoroacetophenone affords the *S* alcohol



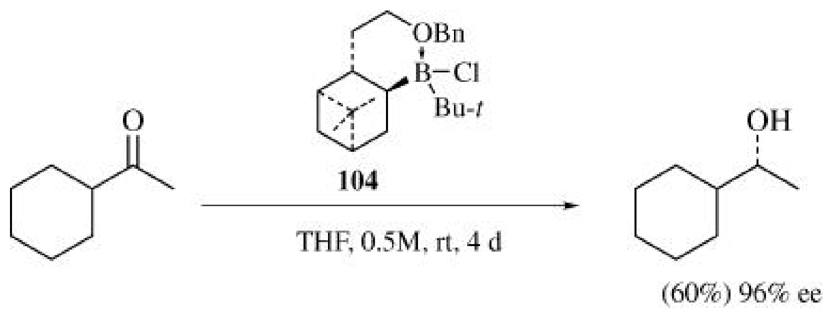
(99)

in 90% ee. The optical purity of 1-phenyl-2,2,2-trifluoroethanol is upgraded to > 99% ee by crystallization from pentane. Modified versions of **102** with alkyl groups of varying steric requirements have been prepared. (165, 166) Reagent **103** achieves 96% ee in the asymmetric reduction of acetophenone (Eq. 100). (165) The

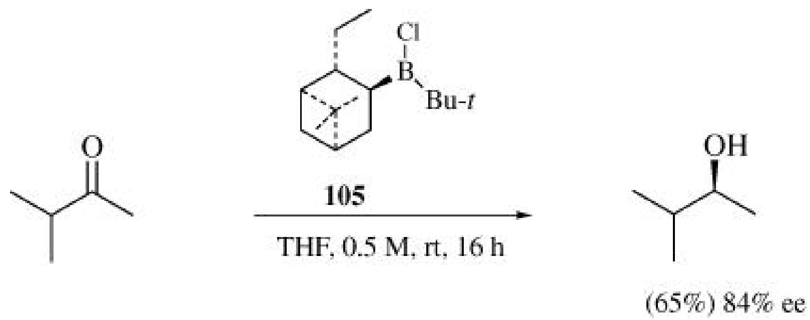


(100)

product possesses the *R* instead of the *S* configuration obtained from **102**. This agent reduces 2-chloroacetophenone and 3-acetylpyridine to the *R* alcohols in 98% and 96% ee, respectively. Although the reduction of dialkyl ketones with **102** proceeds in relatively low ee, significant improvement is achieved by using **104** (Eq. 101) or **105** (Eq. 102). (166) Hydroboration of 2-ethylapopinene with

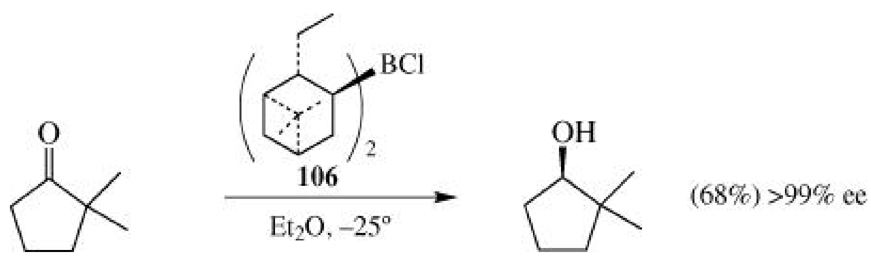


(101)



(102)

chloroborane-methyl sulfide gives *B*-chlorodiiso-2-ethylapopinocampheylborane **106**, which reduces prochiral ketones of intermediate steric requirements to the alcohols in high ee (Eq. 103). (170) The chloroalane **107** can also be used for the reduction of ketones (Eq. 104). (171)



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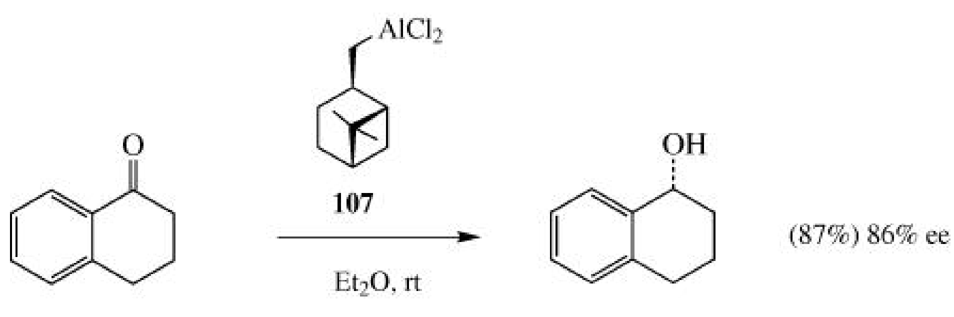


(104)

2.5. Transition Metal Catalyzed Reductions

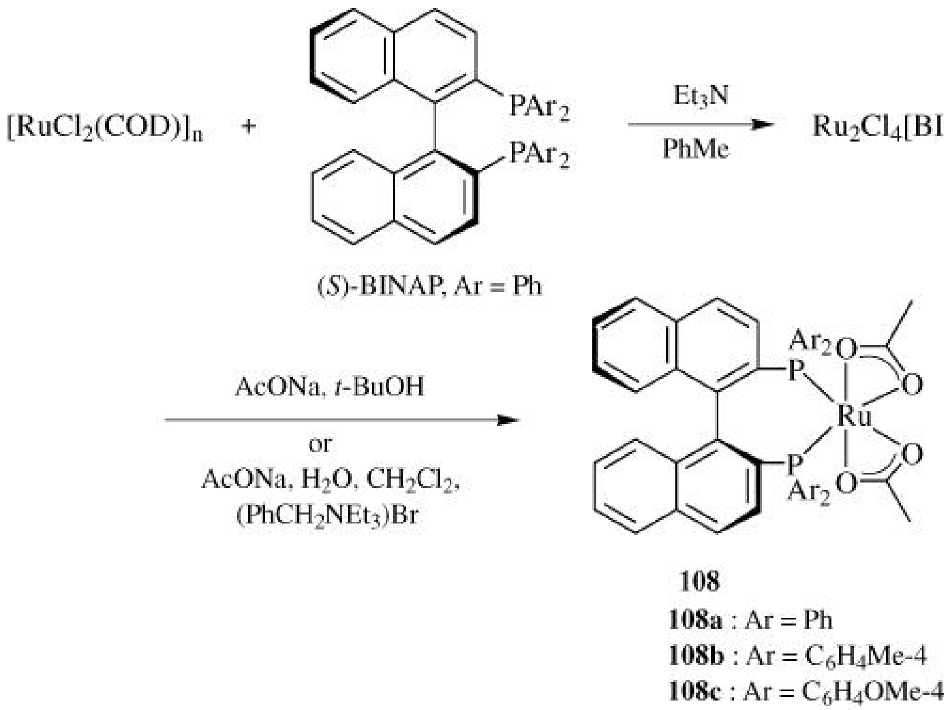
Hydrogenation and hydrosilylation of prochiral ketones are catalyzed by chirally modified transition metal catalysts. Recently, many efficient systems have appeared in the literature. From a practical point of view, catalytic asymmetric hydrogenation and hydrosilylation of ketones are among the most important methodologies for obtaining enantioenriched alcohols. Several review articles on the transition metal catalyzed reduction of ketones have appeared recently. (172, 173)

2.5.1. Hydrogenation

Rh, Ru, and Ir complexes of enantiopure diphosphine ligands have been used as catalysts for asymmetric hydrogenation of various kinds of C = C,C = O, and C = N double bonds. Although much success in asymmetric hydrogenation of C = C has been obtained, early studies of asymmetric hydrogenation of ketones gave disappointing results. (174-179) Recently, highly enantioselective reductions of aromatic ketones have been realized with some complexes of Rh and Ir and enantiopure nitrogen ligands.

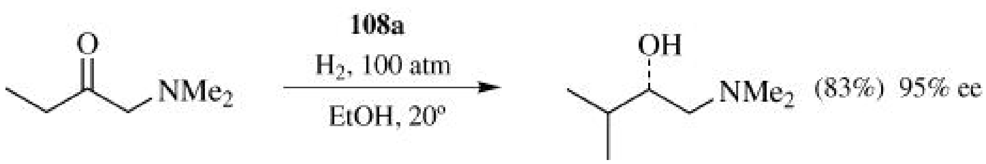
2.5.1.1. Amino Ketones

Asymmetric hydrogenation of α -amino ketones has been achieved by using enantiopure Ru and Rh complexes. Among the most efficient chiral ligands for the asymmetric reduction of ketones are 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (**108a**), and its derivatives. (180) The enantiopure Ru complexes



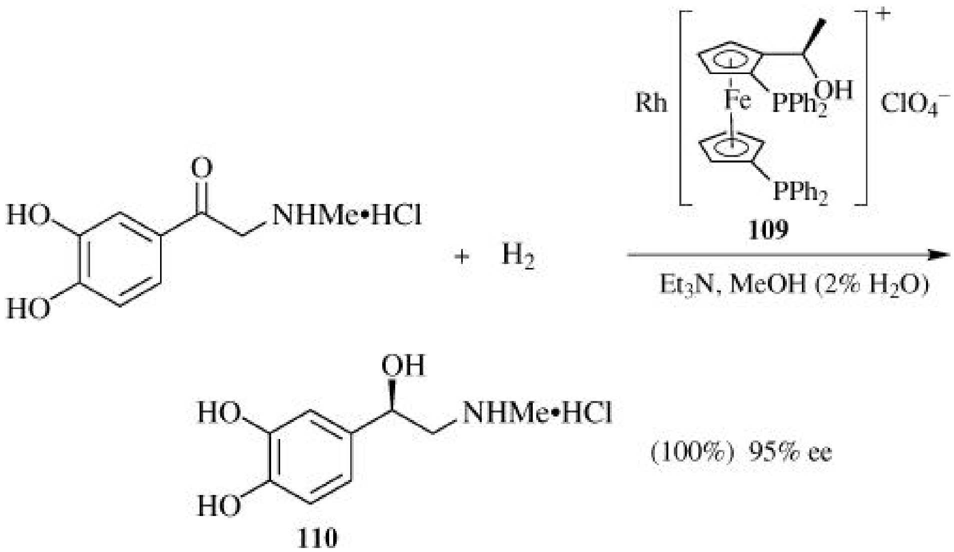
(105)

108, prepared according to Eq. 105, effect the hydrogenation of amino ketones with excellent levels of enantioselection (Eq. 106). (181)



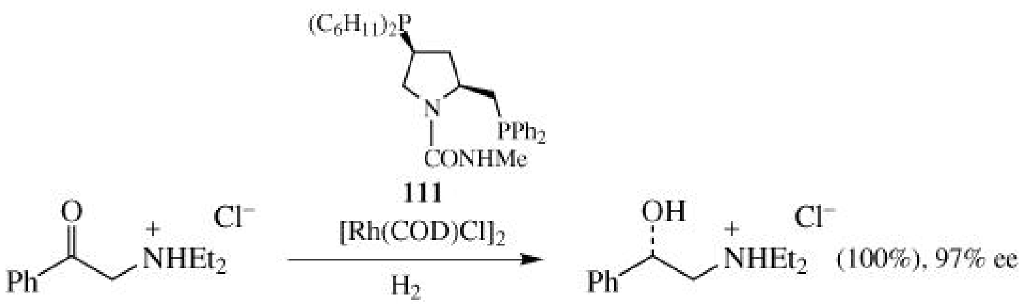
(106)

The key factor in stereodifferentiation is the simultaneous coordination of the carbonyl oxygen and heteroatom nitrogen to the Ru atom to make a 5-membered chelate ring. (182) The Rh complex of an enantiopure (hydroxyalkylferrocenyl)-phosphine (**109**) brings about hydrogenation of amino ketones to give amino alcohols such as epinephrine **110** (Eq. 107). (174) The enantiopure diphosphine **111** is

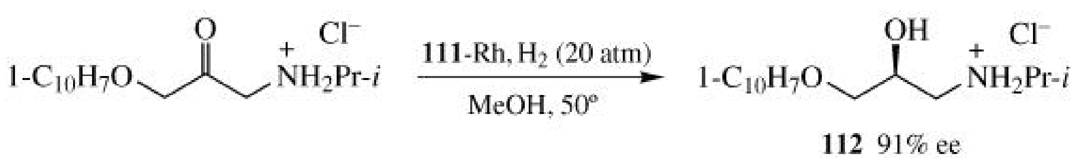


(107)

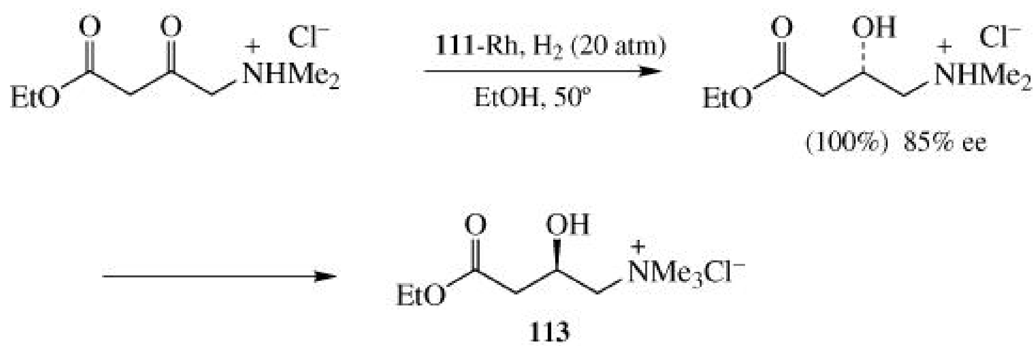
also effective for the Rh-catalyzed asymmetric hydrogenation of amino ketones (Eq. 108). (183, 184) This method has been applied to the synthesis of several enantioenriched amino alcohol derivatives such as (*S*)-propranolol hydrochloride (**112**) (Eq. 109), (185) (*R*)-norcarnitine (**113**) (Eq. 110), (186) fluoxetine hydrochloride



(108)



(109)



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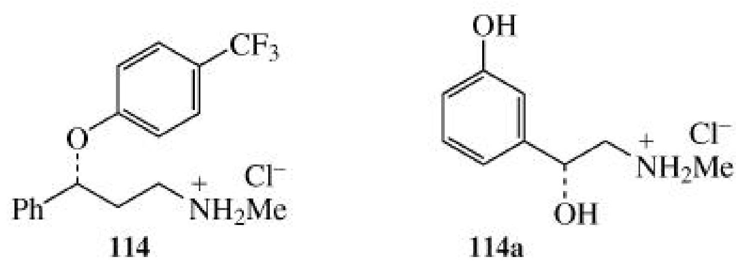
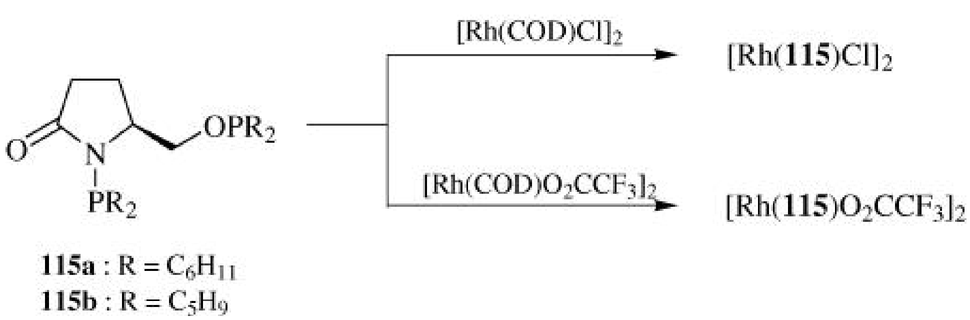
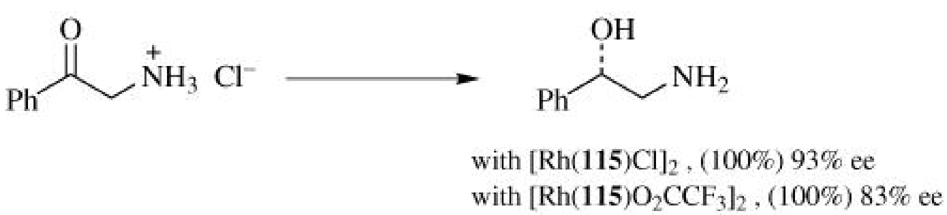


(**114**), (187) and phenylephrine hydrochloride (**114a**). (184) The amido-phosphine-phosphinites enantiopure ligands **115** (Eq. 111) are efficient for the asymmetric reduction of 2-aminoacetophenone (Eq. 112). (188)



(111)



(112)

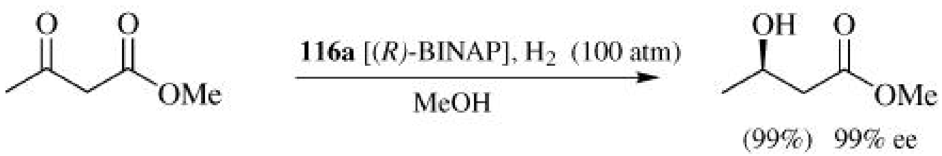
2.5.1.2. Keto Esters

Highly enantioselective hydrogenation of α - or β -keto esters is achieved with some Ru catalysts. The BINAP-Ru diacetate complexes **108**, which give high ee in the hydrogenation of various olefins, are ineffective in the hydrogenation of methyl 3-oxobutanoate. However, addition of 2 equivalents of hydrochloric acid dramatically enhances the rate of the reaction and results in excellent enantioselectivity (Eq. 113). (189) These halogen-containing complexes with the empirical

108a + 2 HX ⟶ $[RuX_2(BINAP)]$ (113)

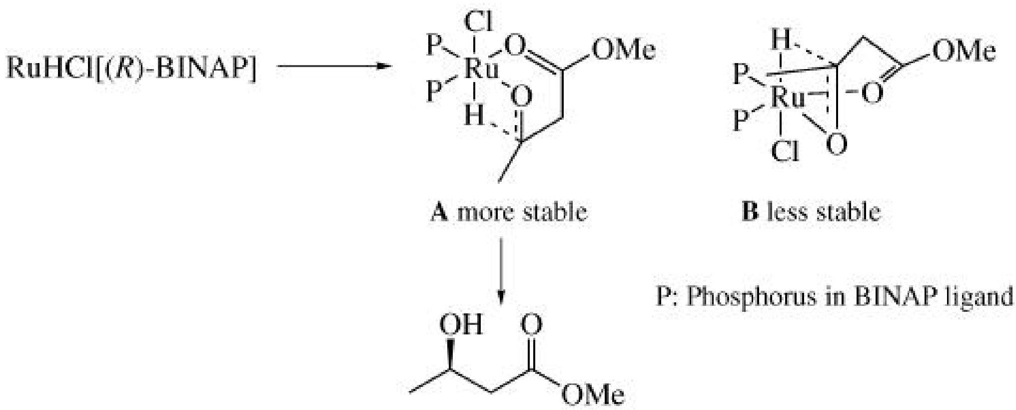
116a, X = Cl
116b, X = Br

formula RuX_2(BINAP) (X = Cl, Br, I) are excellent catalysts for reduction of keto esters (Eq. 114). Hydrogenation proceeds smoothly in methanol at



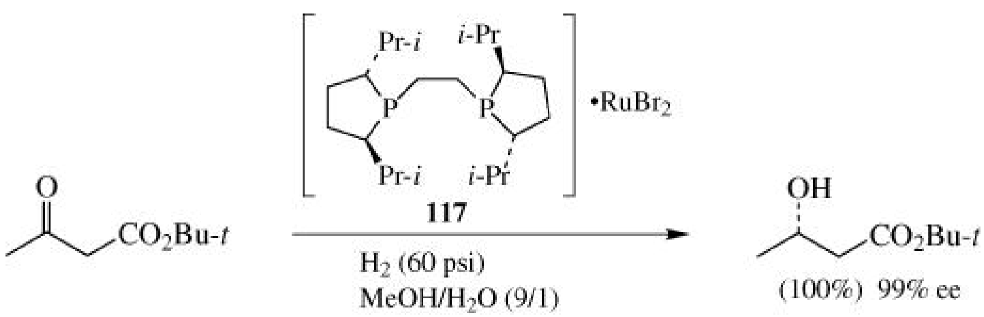
(114)

room temperature at an initial pressure of 3–100 atm. Methyl 3-oxobutanoate is hydrogenated to the corresponding hydroxy ester in 99% ee and 99% yield at a substrate/catalyst mole ratio (s/c) of 1800. Even when the s/c is 10,000, the same product is obtained in 98% yield and 96% ee. Intermediates in the hydrogenation of keto esters might be five- or seven-membered chelate complexes in which the Ru(II) atom interacts with the carbonyl oxygen and oxygen of the ester group. (*S*)-BINAP-Ru(II) catalyst affords *S* alcohols predominantly, whereas the *R* catalyst gives the *R* enantiomers preferentially. This hydrogenation seems to occur by the monohydride mechanism. (190, 191) Upon exposure to hydrogen, $RuCl_2$(BINAP) loses chloride to form a RuHCl species, which reversibly forms the keto ester complex. The transition state **A** derived from (*R*)-BINAP catalyst is much more stable than its diastereomer **B**. The *R* alcohol is generated from transition state **A** (Eq. 115).

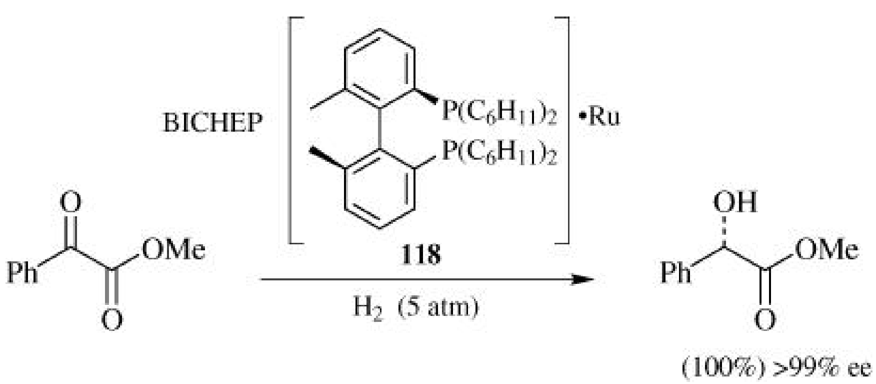


(115)

Bis(phospholane) ligands such as 1,2-bis(*trans*-2,5-dialkylphospholano)ethane (**117**) also achieve highly enantioselective Ru-catalyzed hydrogenation of β -keto esters under mild conditions (Eq. 116). α -Keto carboxylic acid derivatives are reduced with BICHEP **118**-Ru catalyst with up to 99% ee (Eq. 117).

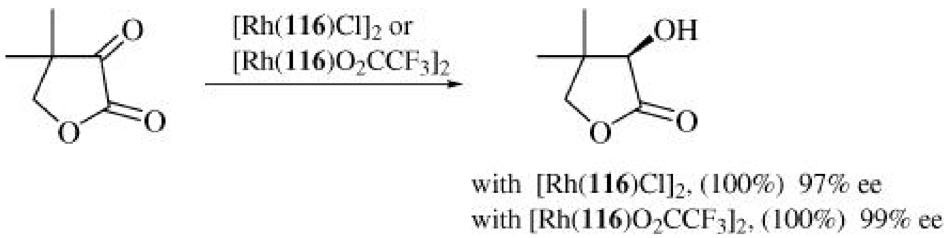


(116)



(117)

Rh catalysts [Rh(**116**)Cl]$_2$ and [Rh(**116**)O$_2$CCF$_3$]$_2$, which are efficient catalysts in the reduction of amino ketones, show high efficiency in the reduction of ketopantolactone (Eq. 118) and *N*-benzylphenylglyoxamide. (188) Silica-supported Rh

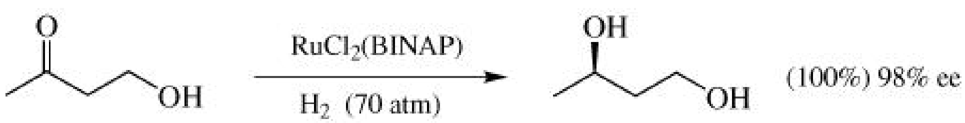


(118)

complexes have also been synthesized and tested as catalyst precursors for the enantioselective hydrogenation of keto esters and keto amides. (192)

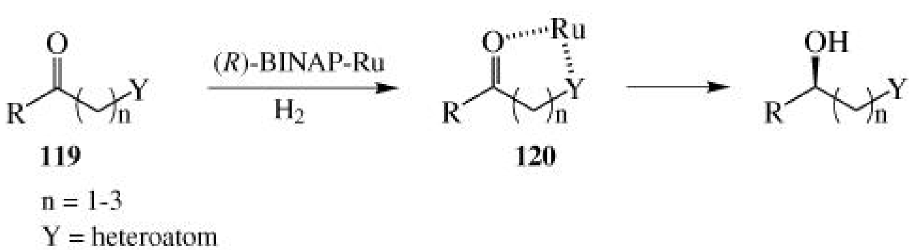
2.5.1.3. Other Functionalized Ketones

The BINAP-Ru catalysts are also extremely efficient for the asymmetric hydrogenation of various functionalized ketones such as hydroxy, alkoxy, and siloxy ketones; keto amides; diketones, and keto carboxylic acids. (181, 193) For example, 1-hydroxy-3-butanone is reduced to the corresponding enantioenriched diol in 98% ee (Eq. 119). In the case of the functionalized



(119)

ketones **119**, a simultaneous coordination of the carbonyl oxygen and heteroatom Y to Ru may be important at the enantiodifferentiation step (Eq. 120).

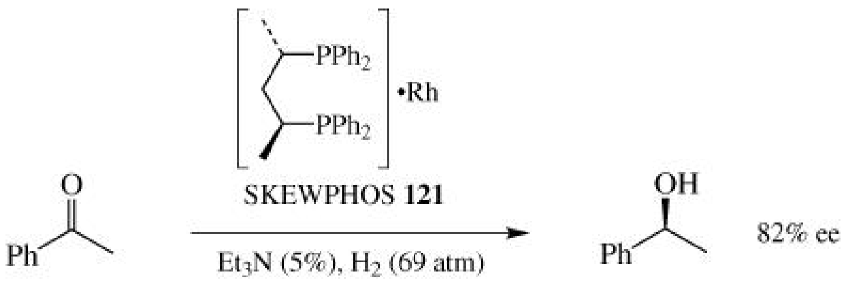


(120)

The general sense of asymmetric induction in the hydrogenation suggests that cyclic structure **120** may be the key intermediate.

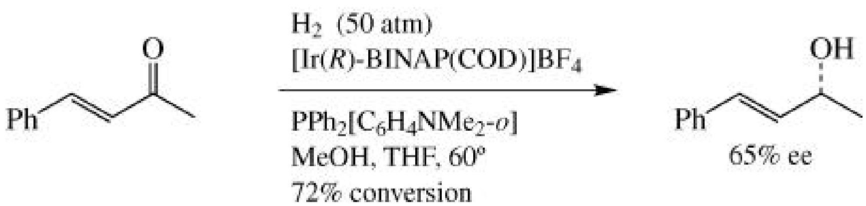
2.5.1.4. Simple Ketones

Ruthenium catalysts such as halogen-containing BINAP-Ru(II), which exhibit high chiral recognition in the hydrogenation of functionalized ketones, do not achieve high enantioselection with simple ketones. Since simple ketones have only one carbonyl oxygen that can coordinate to Ru, it is difficult to control catalyst orientation. Indeed, high enantioselectivity in the hydrogenation of simple ketones is still difficult to realize, although some exceptions were recently reported. For example, in the hydrogenation of acetophenone, a SKEWPHOS catalyst (**121**)-Rh(I) gives the best results (82% ee) (Eq. 121). (194) Hydrogenation



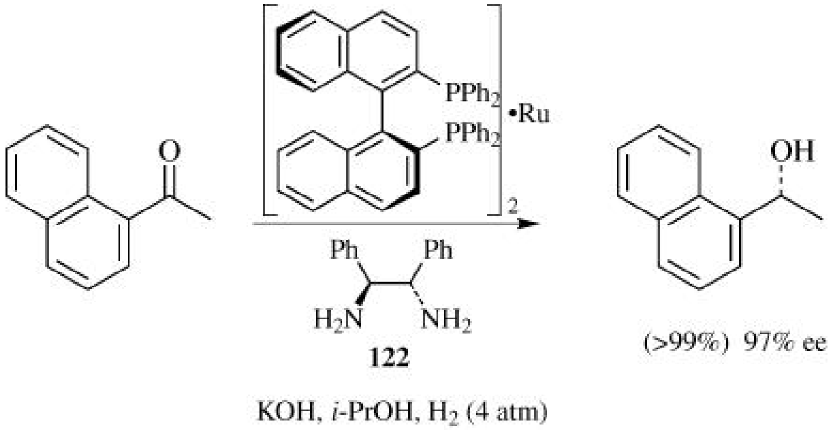
(121)

of (*E*)-benzalacetone is catalyzed by [Ir(BINAP)(COD)]BF_4 in the presence of an aminophosphine to give the allylic alcohol in 65% ee at 72% conversion (Eq. 122). (195) Phosphine-Ru(II) complexes are normally not very active as



(122)

catalysts for hydrogenation of simple ketones as noted above. The activity of $RuCl_2[PPh_3]_3$ is remarkably enhanced by the addition of 1 equivalent of ethylenediamine. The asymmetric hydrogenation of 1′-acetonaphthone with a catalyst system consisting of $RuCl_2$-[(*S*)-BINAP]$(DMF)_n$, (*S,S*)-1,2-diphenylethylenediamine (**122**), and KOH in 2-propanol affords (*S*)-1-(1-naphthyl)ethanol in 97% ee and in > 99% yield (Eq. 123). (196)



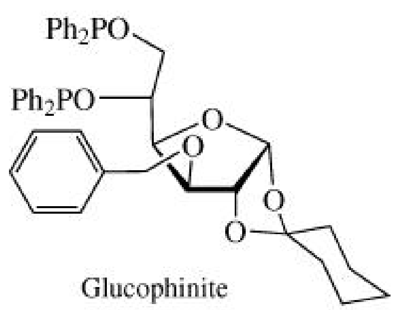
(123)

2.5.2. Hydrosilylation (197)

Addition of a Si-H group to a ketone carbonyl produces a silyl ether that can be easily hydrolyzed to the corresponding alcohol. Rhodium catalysts bearing chiral phosphine ligands have been used for the asymmetric hydrosilylation of many ketones (Eq. 124). Most of the chiral phosphine-rhodium

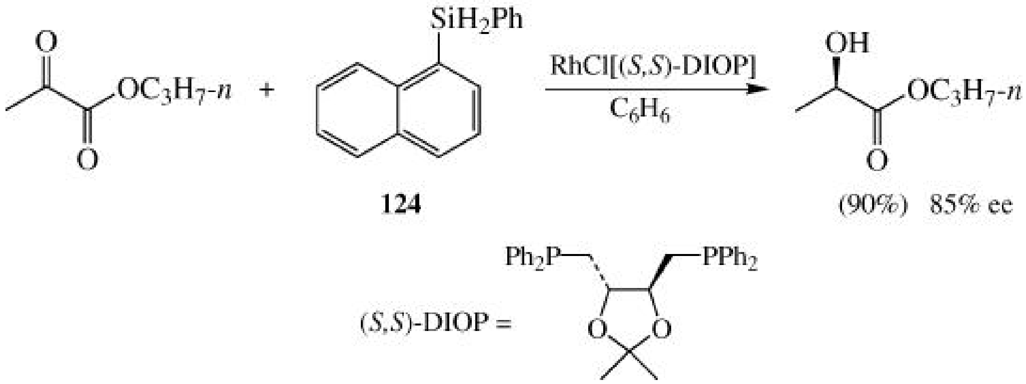
(124)

catalysts developed prior to the early 1980 s afford only low-to-moderate enantioselectivities. For example, the glucose-derived enantiopure catalyst [glucophinite (**123**)-Rh(COD)]BF_3 gives the best result in the reduction of acetophenone

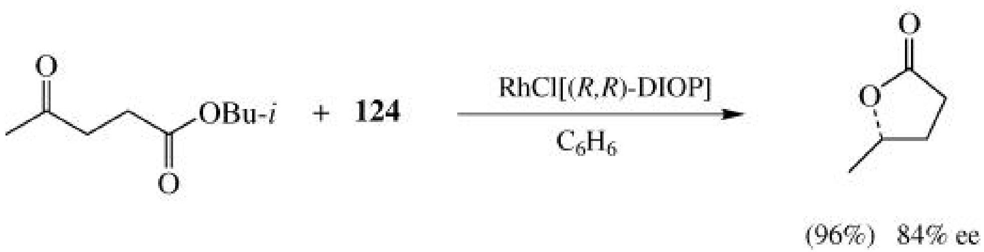


123

(65% yield, 65% ee) with 1-naphthylphenylsilane. (198) The use of 1-naphthyl-phenylsilane (**124**) gives higher enantioselectivity than diphenylsilane in many hydrosilylations using enantiopure phosphine ligands. In the hydrosilylation of α - and γ -keto esters, high enantioselectivity (85% ee) is reported using the enantiopure catalyst [DIOP -Rh(COD)Cl]$_2$ (Eqs. 125, 126). (199, 200) However, β -keto esters



(125)



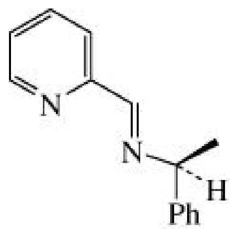
(126)

such as acetoacetate and benzoylacetate do not give asymmetric inductions above 70% ee with this system. The enantioselectivities in the hydrosilylation of α , β -unsaturated ketones are lower than 50% ee. Thus the complexes of Rh with enantiopure phosphine ligands show limited success in the enantioselective hydrosilylation of ketones.

The nitrogen-containing ligands **125** and **126** were synthesized from 2-pyridinecarboxaldehyde and enantiopure 1-phenethylamine and 3-aminomethylpinane. The enantiopure iminopyridine derivatives were used as ligands for Rh in the hydrosilylation of ketones. Acetophenone is reduced with diphenylsilane in the presence of the Rh complex with **127** to give 1-phenylethanol in 79% ee. (201, 202)

Enantiopure nitrogen ligands pyridinethiazolidine (PYTHIA) **127** were prepared from L-cysteine and used as chiral ligands for Rh. The asymmetric hydrosilylation of ketones with [Rh(COD)Cl]$_2$ using a large excess of **127c** proceeds smoothly to give the alcohol in 98% ee. (203-205) Using this chiral catalyst, various ketones are reduced with silanes to give enantioenriched alcohols. The chiral ligands **127a** and **127b** also induce high enantioselectivities in this system. The use of 1-naphthylphenylsilane instead of diphenylsilane decreases the enantioselectivity in this system.

Oxazoline-containing enantiopure nitrogen ligands can be used for the asymmetric hydrosilylation of ketones. (206) The chirality of the oxazoline ring is derived from readily available enantiopure β -amino alcohols. Using the enantiopure ligand **128**, diphenylsilane reduces acetophenone in the presence of $[Rh(COD)Cl]_2$ to give 1-phenylethanol in 60–91% ee. (207, 208) The similar enantiopure ligand **129** is also effective for the asymmetric hydrosilylation of acetophenone to give 1-phenylethanol with 80% ee. (209)



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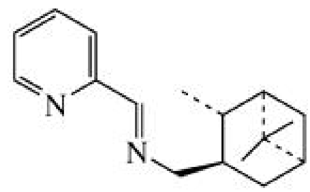
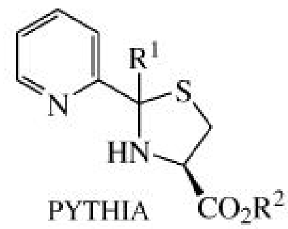
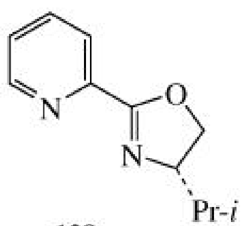


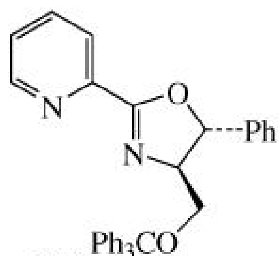
126



127a; R^1 = H, R^2 = Me
127b; R^1 = Me, R^2 = Me
127c; R^1 = H, R^2 = Et

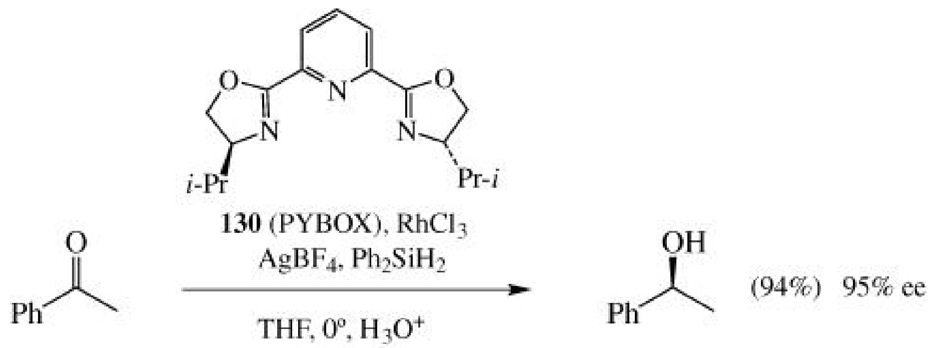


128



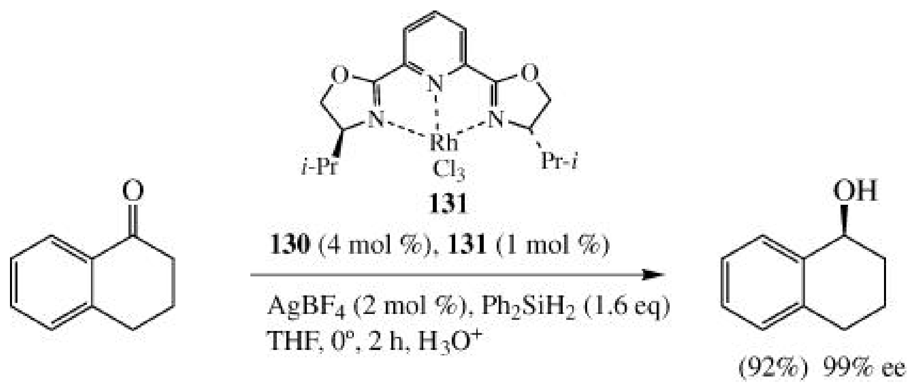
129

A well-designed C_2 symmetrical pyridine bisoxazoline ligand **130** (PY BOX) has been introduced for the hydrosilylation of simple ketones. These terdentate chiral ligands are readily prepared by the condensation of pyridine-2,6-dicarboxylic acid and enantiopure β -amino alcohols. Acetophenone is hydrosilylated with diphenylsilane by using a Rh(III) complex **131** in 76% ee. The use of the cationic complex obtained by treatment with $AgBF_4$ increases enantioselectivity to 83% ee. Good results are obtained by use of an equimolar amount of chiral nitrogen ligand with respect to Rh. Further improvement is achieved by using a 4-fold excess of chiral ligand **130** to give 1-phenylethanol in 94% yield and 95% ee (Eq. 127). (210) The enantioselective reduction of other simple ketones proceeds



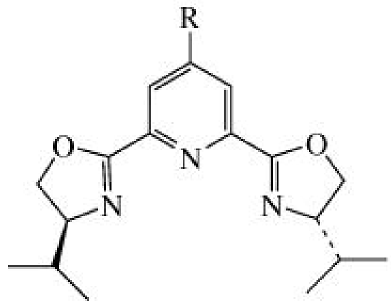
(127)

using the PYBOX-Rh system. The hydrosilylation of propiophenone, α -naphthyl methyl ketone, β -naphthyl methyl ketone, and α -tetralone results in enantiomeric excesses of 91%, 94%, 93%, and 99%, respectively (Eq. 128). The reduction of

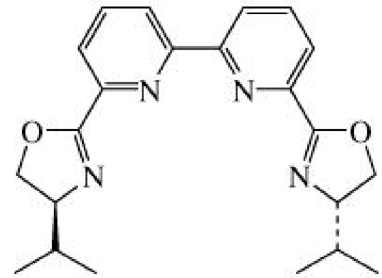


(128)

α , β -unsaturated ketones with this system gives the enantioenriched allylic alcohols. In the hydrosilylation of chalcone, 1,2-reduction takes place at 0° to give chalcol in 87% yield and 71% ee. Substituents at the 4 position on the oxazoline ring of the PY BOX ligand affect not only the enantioselectivity but also the reaction rate. Of the various ligands tested in the reduction of acetophenone, the isopropyl group gives the best result. Substituents at the 4 position of the pyridine skeleton of the PY BOX ligand also influence both selectivity and reactivity. The asymmetric hydrosilylation of acetophenone proceeds at 20° for 6 hours with 91% ee in the presence of the rhodium chloride complex of **132a**, which has an electron-donating group, whereas the use of **132c**, with an electron-withdrawing group, enhances the reaction rate (–5°, 3 hours) and 83% ee 1-phenylethanol is obtained. (211) Another chiral nitrogen ligand, bis(oxazolinyl)bipyridine **133**, has been used for the asymmetric reduction of ketones. (212) The enantiopure rhodium catalyst prepared from **133** gives (*S*)-1-phenylethanol in 98% yield and 90% ee.

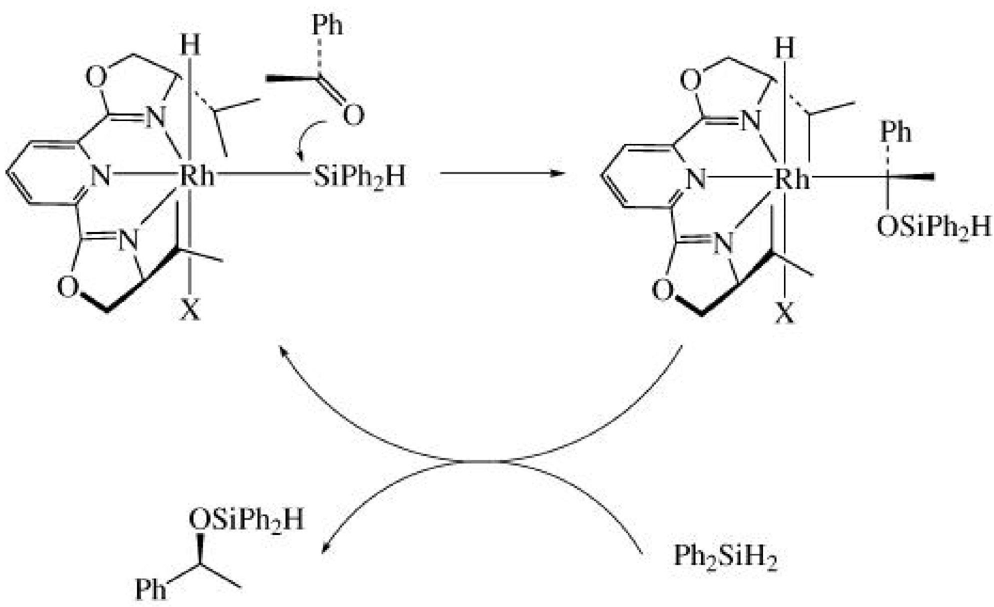


132a; R = Me_2N
132b; R = MeO
132c; R = Cl



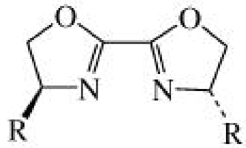
133

Although the reaction pathway for rhodium-catalyzed asymmetric hydrosilylation is unclear, a mechanism involving initial formation of a hydrosilyl-Rh complex has been suggested. (213) The ketone carbonyl inserts into the Rh-Si bond followed by reductive elimination to give the product. With the PYBOX system, the *re* prochiral face of the ketone can be specifically recognized to give the *S* alcohol predominantly (Eq. 129).

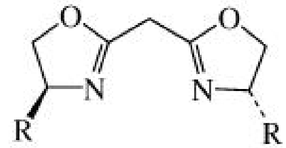


(129)

Other C_2 chiral bidentate oxazoline ligands such as **134** and **135** have been synthesized from oxalic acid and malonic acid. (214) The benzyl derivative **134b** is

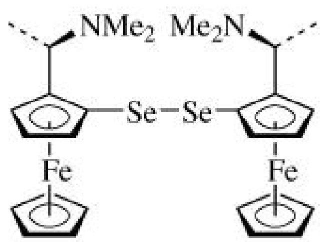


134
134a R = *i*-Pr
134b R = Bn

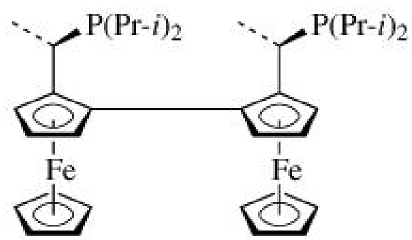


135
135a R = *i*-Pr
135b R = Bn

an effective chiral ligand for a rhodium catalyst in the asymmetric hydrosilylation of acetophenone with diphenylsilane. High enantioselectivity (84% ee, *R*) is obtained when a tenfold excess of the chiral ligand is used. However, isopropyl derivatives **134a** and **135a** show no asymmetric induction in hydrosilylation. Diselenoferrocenylamine **136** is another enantiopure diamine ligand for the hydrosilylation of acetophenone to give the alcohol in 88% ee. (215)

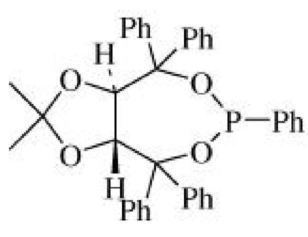


136



137

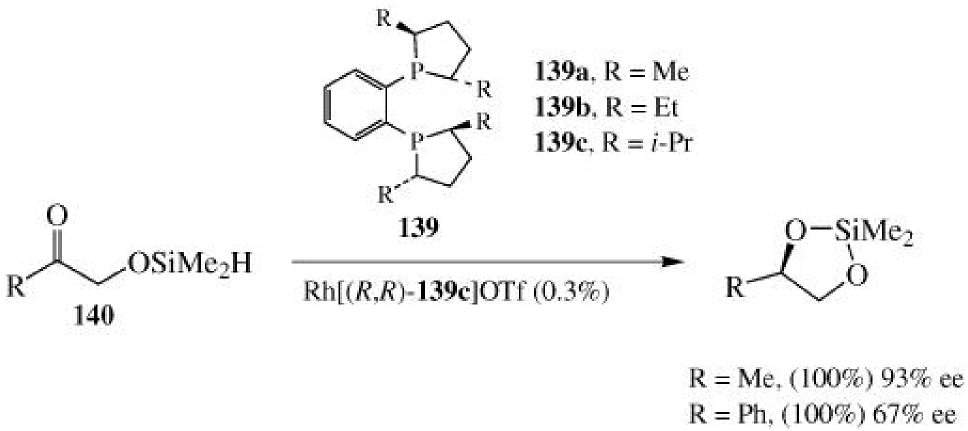
Recently, new enantiopure phosphine ligands have been developed for the hydrosilylation of ketones. The highest enantioselectivity (92% ee) in the reduction of acetophenone is attained by using TRAP **137**. (216) TADDOL derivative **138** is



138

also effective for the reduction of 2-naphthyl methyl ketone (87% ee). (217) An enantiopure diphosphine ligand **139** has been used for the intramolecular hydrosilylation of certain α -siloxy ketones with high selectivity. Reaction of

3-dimethylsiloxy-2-propanone **140** with the catalyst derived from **139c** produces an (*R*)-1,2-diol derivative in 93% ee (Eq. 130). (218)



(130)

2.6. Enzymatic and Related Reductions

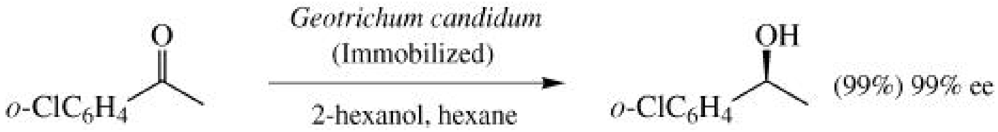
Various alcohol dehydrogenases have been used as chiral catalysts for the reduction of prochiral ketones. (219, 220) Enzymatic methods of reduction take place under mild reaction conditions, minimizing such problems as racemization, isomerization, and rearrangement. Enzymatic reduction of ketones having other functional groups usually proceeds without protection.

2.6.1. Baker's Yeast Mediated Reductions

Utilization of baker's yeast in the asymmetric reduction of ketones has been widely studied. (220) Baker's yeast mediated reduction is strongly dependent on the substrate structure. From 2-hexanone, (*S*)-2-hexanol is obtained in 82% ee, while 3-heptanone is converted to (*R*)-3-heptanol in 27% ee. (221) Recently, stereochemical control in baker's yeast redox biotransformations of aryl methyl ketones to carbinols has been achieved. In the presence of glucose (2.5%), the reduction of acetophenone gives the *R* alcohol in 90% yield with > 95% ee (Eq. 131). (222) These ketones are also reduced by immobilized

(131)

Geotrichum candidum in hexane in the presence of 2-hexanol to afford the alcohols with almost perfect enantioselectivity (Eq. 132). (223) Ketones containing



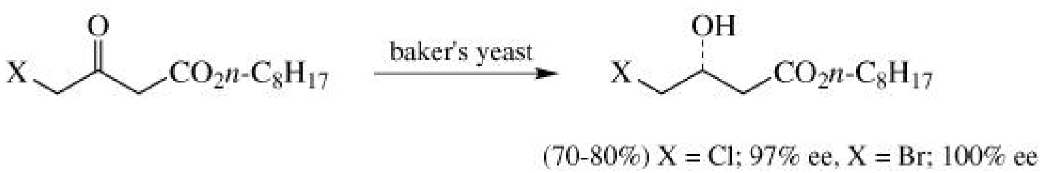
(132)

an olefinic double bond are reduced by baker's yeast to the corresponding unsaturated alcohols in high ee. (224)

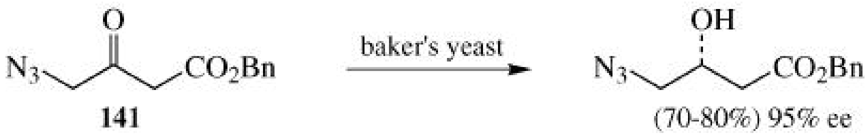
The asymmetric synthesis of β -hydroxy esters from β -keto esters using baker's yeast has been studied extensively. The structure of the ester is an important factor for enantioselection with baker's yeast reduction. From ethyl 3-oxobutanoate the corresponding *S* alcohol is obtained in 88–97% ee (Eq. 133), (225-227)

(133)

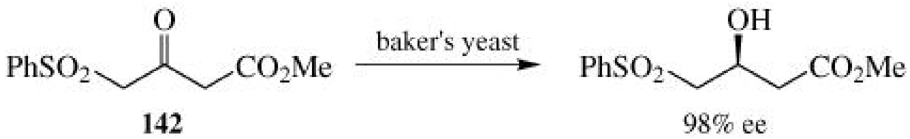
while the *R* alcohol is obtained from ethyl 3-oxopentanoate reduction. (228) β -Keto esters are also reduced asymmetrically by immobilized baker's yeast. (229) A substituent in the γ position can dramatically influence the sense of the asymmetric induction. Octyl γ -chloroacetoacetate and γ -bromoacetoacetate yield the *S* alcohol in 97% ee and 100% ee, respectively (Eq. 134), while the *R* alcohol is obtained in 100% ee from ethyl γ -bromoacetoacetate. (230) Azide **141** (Eq. 135) and sulfone **142** (Eq. 136) (231) are reduced with excellent enantioselectivities. Reduction



(134)



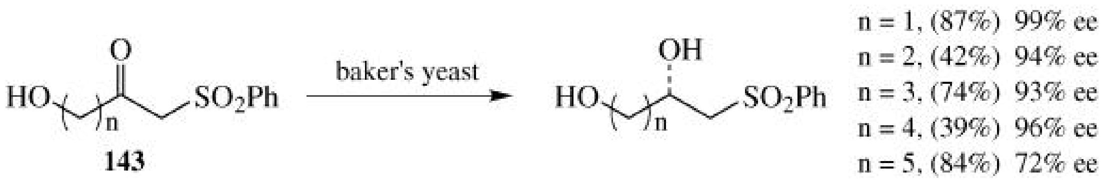
(135)



142 (136)

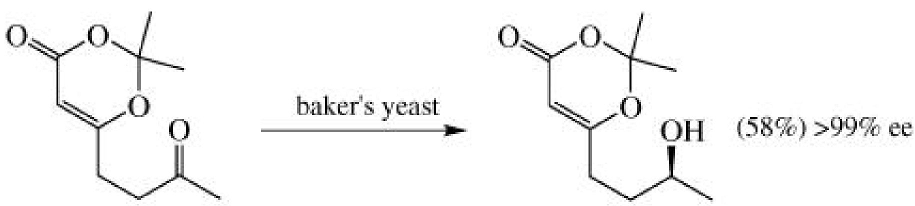
of cyclic keto esters also proceeds with high selectivity. (232-236) β -Keto dithioesters also give high asymmetric inductions. (237)

Hydroxy β -keto sulfones **143** are reduced with baker's yeast to give the corresponding alcohols in high enantioselectivities (Eq. 137). (238) Baker's yeast reduction



143 (137)

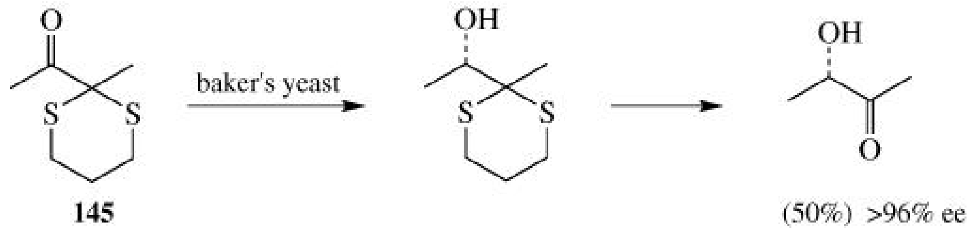
is also effective for γ - and δ -ketocarboxylic acids and δ -ketoesters. (239, 240) Prochiral methyl ketones **144** carrying the 6-(4-oxo-1,3-dioxinyl)group are reduced to the corresponding alcohols in high ee (Eq. 138). (241) Reduction of α -hydroxy ketones



144 (138)

provides enantioenriched diols with excellent enantioselectivity. (242-244) For several baker's yeast reductions, it is possible to improve or invert the enantioselectivity by simple substrate manipulations as shown for β -keto esters.

Diketones or keto aldehydes in which one carbonyl group is protected can also be reduced asymmetrically to the corresponding alcohols (Eq. 139). (240, 245) Baker's



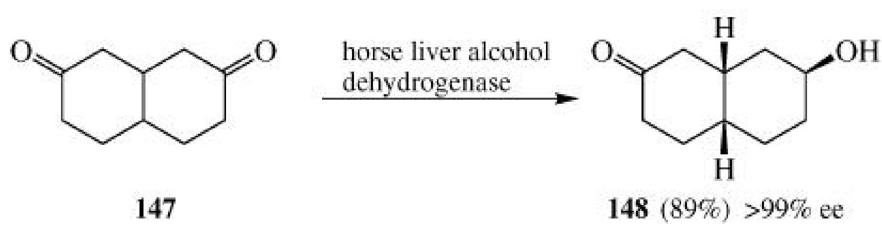
(139)

yeast reduction of α -keto thioacetals **145** yields enantioenriched α -hydroxy thioacetals, which are equivalents of α -hydroxy aldehydes and ketones. Several glyceraldehyde derivatives such as **146** are enantioselectively synthesized by baker's yeast mediated reduction of protected ketones (Eq. 140). (245) Asymmetric

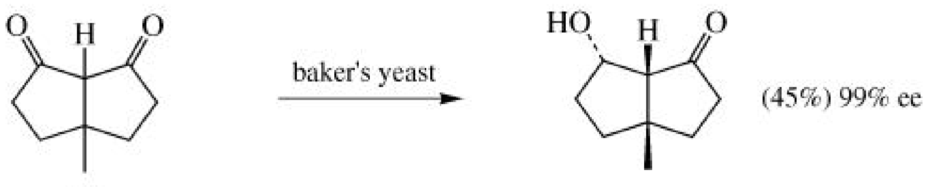
(140)

reduction of β -keto thioacetals is achieved by using baker's yeast, *Aspergillus niger*, or *Geotrichum candidum*. (246)

Hydroxy ketone **148** is a natural product synthon, not readily available via traditional chemical methods. Enantioenriched **148** is obtained in good yield by reduction of **147** with commercially available horse liver alcohol dehydrogenase (Eq. 141). (247, 248) Baker's yeast is also effective for the enantioselective reduction of σ -symmetrical bicyclic diketone **149** (Eq. 142). (249)



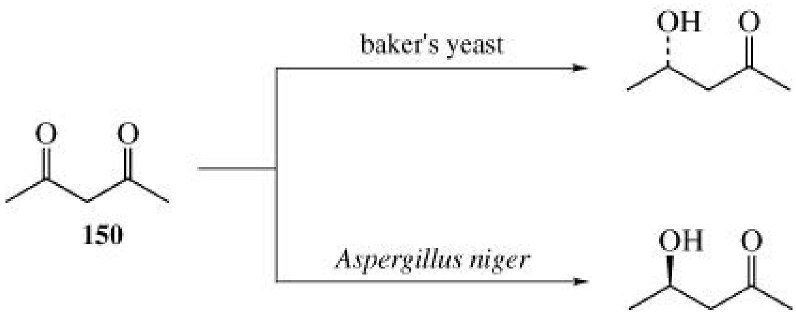
(141)



149

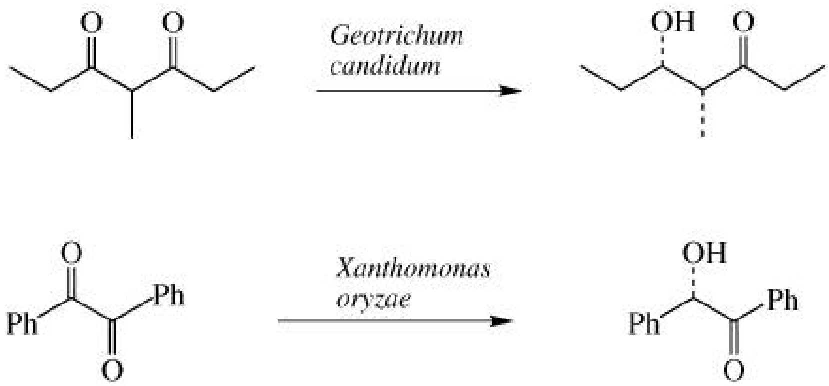
(142)

The simple diketone **150** is reduced with baker's yeast to give an (*S*)-hydroxy ketone (Eq. 143). With microorganisms other than baker's yeast, the same substrate is reduced with opposite stereochemistry (Eq. 143). (250) Other diketones are reduced to the enantiopure hydroxy ketones by the use of microorganisms as shown in Eq. 144. (251-253)



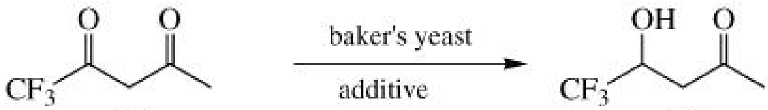
150

(143)



(144)

Baker's yeast reduction of fluorinated β -diketones **151** gives the corresponding ketols **152**. The presence of additives such as allyl alcohol, methyl vinyl ketone, and allyl bromide affects the stereochemistry of the reaction (Eq. 145). (254)



151 → 152

Additive		% ee
—	(97%)	72 (*S*)
allyl alcohol	(82%)	92 (*S*)
methyl vinyl ketone	(82%)	86 (*S*)
allyl bromide	(37%)	81 (*R*)

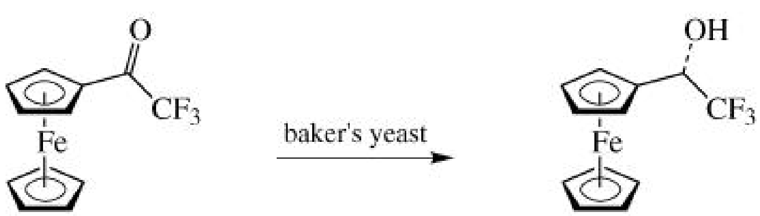
(145)

Enantioenriched α -phenylpyridylmethanols are synthesized by baker's yeast reduction of the corresponding ketones (Eq. 146). (255) Asymmetric reduction of 2-benzoylpyridine by immobilized baker's yeast in hexane has been achieved to give the alcohol in high optical purity (96% ee).

(146)

free baker's yeast in water, (78%) 86% ee
immobilized baker's yeast in water, (86%) 84% ee
immobilized baker's yeast in hexane (20%) 96% ee

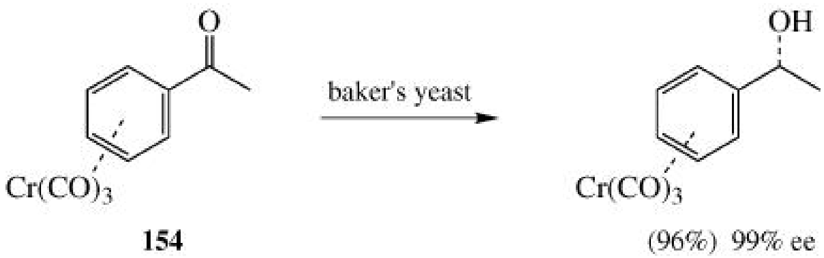
Organometallic ketones such as ferrocenyl (**153**) and arenechromium carbonyl (**154**) ketones can be reduced with baker's yeast (Eqs. 147, 148). (256-258)



153

(91%) >90% ee

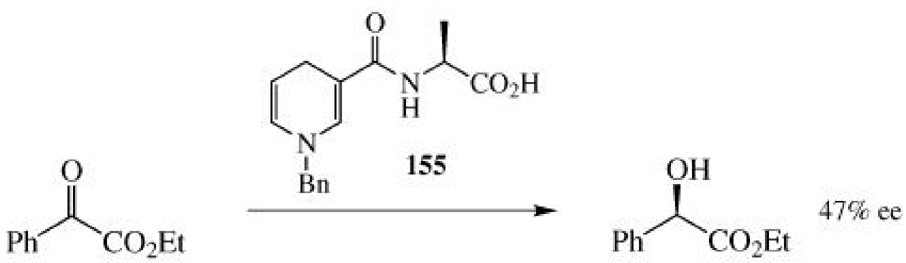
(147)



(148)

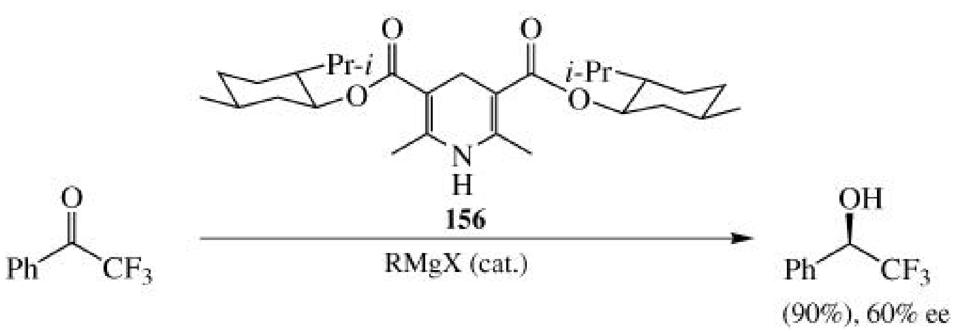
2.6.2. Reduction with Chiral Dihydropyridine Reagents

Many biological reductions are dependent on nicotinamide coenzymes NAD(P)H. Various dihydropyridine derivatives have been prepared and used for ketone reduction. For example, in the reduction of benzoylformate with L-alanine-*N*-benzylnicotinamide (**155**), (*R*)-mandelate is obtained in 47% ee (Eq. 149). (259, 260)



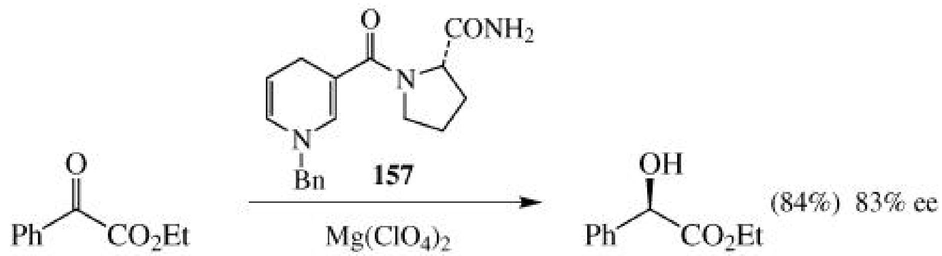
(149)

Di-(*R*)-menthyl ester (**156**) reduction of trifluoroacetophenone is catalyzed by a Grignard reagent to give *R* alcohol in 90% yield and 60% ee (Eq. 150). Asymmetric



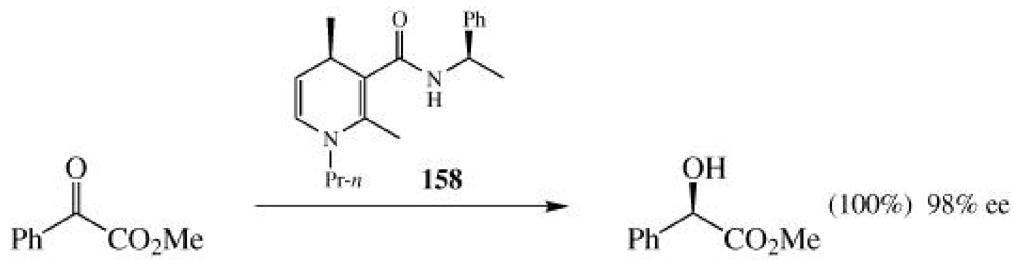
(150)

reduction of benzoylformate with *N*-benzyldihydropyridine prolinamide (**157**) in the presence of magnesium perchlorate provides (*R*)-mandelate in 84% yield with 83% ee (Eq. 151). (261) These enantiopure dihydropyridine reagents have two



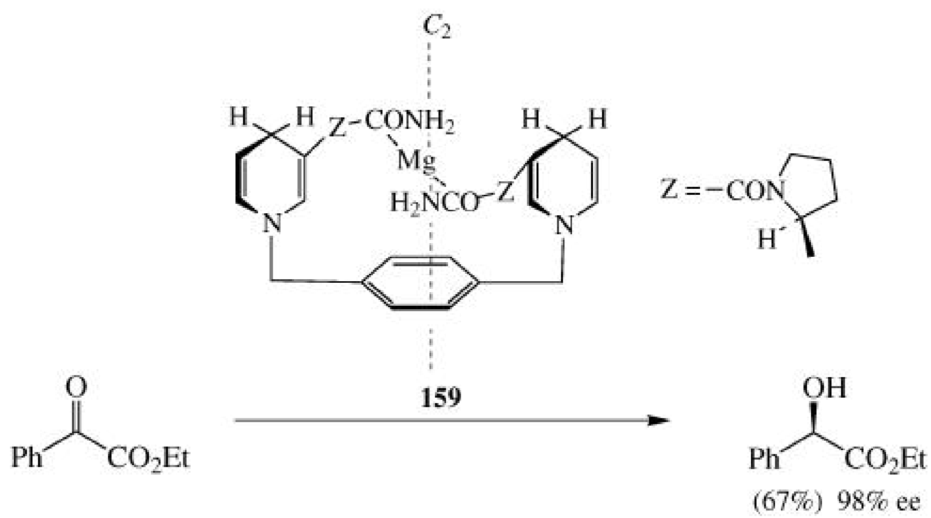
(151)

diastereotopic hydrogens at the 4 position of the dihydropyridine nucleus. Enantiopure nicotinamide reductant **158**, in which one of the hydrogens is replaced by a methyl group, has been used for the asymmetric reduction of various ketones and is highly stereoselective. (262) By using this reagent benzoylformate is reduced to mandelate in 100% conversion with 98% ee (Eq. 152). Other activated ketones



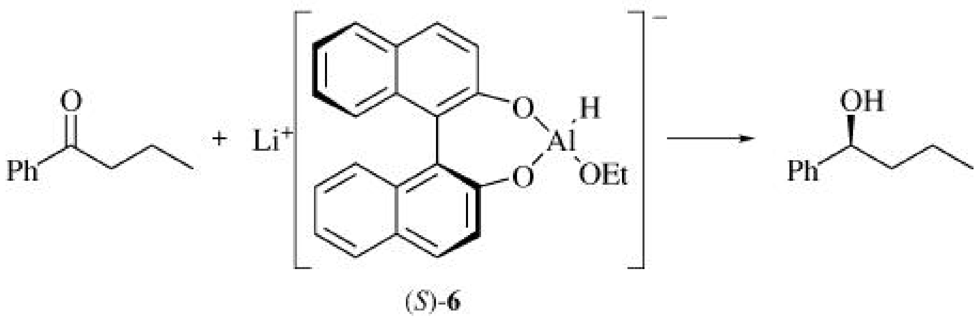
(152)

such as pivaloylformates, trifluoroacetophenone, and acetylpyridine are reduced with this reagent to give the corresponding secondary alcohols with high enantioselectivities. Enantiopure bis(dihydropyridine) derivatives bearing (*S*)-prolinamide, such as **159**, show high efficiency in ketone reduction. Their C_2 symmetry constrains the two equivalent dihydropyridine units into blocking specific faces of each other (Eq. 153). (263)



(153)

3. Experimental Procedures


(154)

3.1. Enantioselective Reduction of Ketones with Chirally Modified $LiAlH_4$ [reduction of Butyrophenone with BINAL-H (6)] (13)

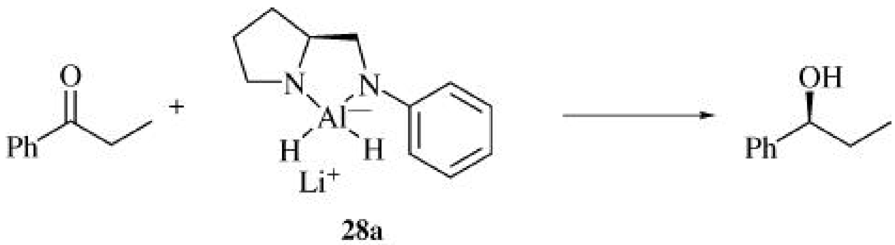
3.1.1.1. Preparation of BINAL-H (6) Reagents

A long-necked flask equipped with a rubber septum was flame-dried and placed under an argon atmosphere. To this a 0.7–2.0 M THF solution of LAH (filtered through dry Celite) was introduced via syringe, and then at room temperature an alcohol in THF (2.0 M, 1 equiv) was added dropwise over a period of ca. 10 minutes with stirring. Subsequently a THF solution of optically pure 2,2¢-dihydroxy-1,1¢-binaphthyl [(*R*)- or (*S*)-**5**] (0.6 M, 1 equiv) was added dropwise, and the resulting mixture was stirred usually for an additional 30 minutes at room temperature and used for the asymmetric reduction.

3.1.1.2. Asymmetric Reduction of Butyrophenone

The BINAL-H reagent, (*S*)-**6** (R′O = EtO), was prepared from LAH (1.63 M THF solution, 5.1 mL, 8.3 mmol), ethanol (2.0 M THF solution, 4.2 mL, 8.4 mmol), and (–)-binaphthol [(*S*)-**5**] (2.4 g, 8.4 mmol) in THF (13 mL). After stirring for 30 minutes at room temperature, the reducing agent was cooled to –100° in a liquid nitrogen-methanol bath. A solution of butyrophenone (370 mg, 2.5 mmol) in THF (2.5 mL) was added dropwise over a period of 8 minutes at –100°. The mixture was stirred for an additional 3 hours at this temperature and at –78° (dry ice bath) for 16 hours. After addition of methanol (1 mL) at –78° the mixture was warmed to room temperature. To this was added 2 N HCl (20 mL) and the mixture was extracted with ether. The organic extract was dried and concentrated. Bulb-to-bulb distillation [150–170° (19 mm Hg)] gave a mixture of unreacted butyrophenone and (*S*)-1-phenylbutanol (375 mg) as a colorless oil (92% yield by GC analysis). Crystalline binaphthol remained in the distillation flask; recovered (*S*)-**5** showed after recrystallization from benzene $[\alpha]^{25}_{D}$ – 34.5° (*c* 1.80, THF). Preparative GC (160°) afforded

(S)-1-phenylbutanol as a crystalline solid: mp 46–47°; $[\alpha]^{22}_{D}$ – 45.2° (c 4.81 benzene), 100% ee.



(155)

3.2. Enantioselective Reduction of Propiophenone with (*S*)-2-(Anilinomethyl)pyrrolidine- $LiAlH_4$ Reagent (43)

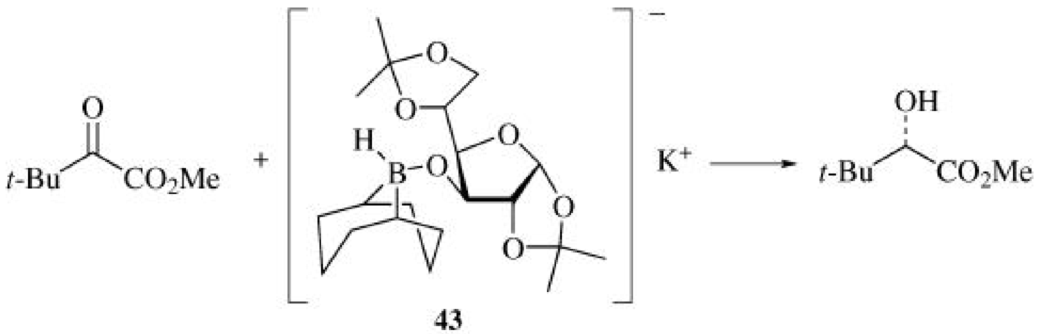
3.2.1.1. (S)-2-(Anilinomethyl)pyrrolidine

(*S*)-*N*-(Benzyloxycarbonyl)prolinanilide (21 g) and 5% Pd-C catalyst (1 g) were stirred vigorously in methanol (120 mL) under a hydrogen atmosphere for 3 hours. The reaction mixture was filtered through Celite and the filtrate was concentrated to give crude (*S*)-prolinanilide, which was recrystallized from cyclohexane to afford pure (*S*)-prolinanilide (11.5 g, 95%, mp 76–77°, $[\alpha]^{27}_{D}$ – 71.0° (c 1.03, EtOH)).

A solution of (*S*)-prolinanilide (10.5 g) in 35 mL of THF was added to a stirring mixture of LAH (4.2 g) in 40 mL of THF at 0° under an argon atmosphere. The reaction mixture was stirred overnight at 0° and hydrolyzed with saturated sodium sulfate solution. After removal of the inorganic material and concentration of the organic layer, fractional distillation under reduced pressure afforded diamine **27a** as a colorless oil (7.2 g, 81%, bp 111–112°/0.55 mm Hg, $[\alpha]^{24}_{D}$19.7° (c 1.09, EtOH); IR 3280 cm^{-1} (NH); ^{1}H NMR($CDCl_3$) δ 0.93–2.13 (m, 5 H), 2.35–3.46 (m, 5 H), 4.10 (br, 1 H), 6.33–6.86 (m, 3 H), 6.86–7.38 (m, 2 H). MS (70 eV) *m/z*, 176 (M^+), 107, 77, 70 and 43.

3.2.1.2. Asymmetric Reduction of Propiophenone

A solution of diamine **27a** (359 mg, 2.04 mmol) in 2 mL of ether was added to a standardized ethereal solution of LAH in ether (2.9 mL, 1.8 mmol) over ten minutes at room temperature under an argon atmosphere. On addition of **27a**, hydrogen gas was evolved and a white precipitate appeared. After stirring for 1 hour at room temperature, a solution of propiophenone (134 mg, 1.00 mmol) in 2 mL of ether was added at – 78°, and the reaction mixture was stirred for 3 hours. The reaction mixture then was hydrolyzed with 0.4 mL of water and washed successively with 8 mL of 0.5 N hydrochloric acid and saturated sodium chloride solution. The ethereal layer was dried over Na_2SO_4 and the solvent was removed. The crude product was purified by preparative TLC to give 1-phenyl-1-propanol (120 mg, 90%), which was further purified for the measurement of specific rotation by bulb-to-bulb distillation (bath temperature 175°/21 mm Hg), and 104 mg of the alcohol was obtained, $[\alpha]^{25}_{D}$ – 23.65° (neat); 85% ee based on the maximum rotation reported. Most of the enantiopure diamine was recovered from the aqueous layer.



(156)

3.3. Enantioselective Reduction of Methyl 3,3-Dimethyl-2-oxobutanoate with Potassium 9-*O*-(1,2: 5,6-di-*O*-isopropylidene- α -D-glucofuranosyl)-9-borabicyclo[3.3.1]nonyl Hydride (43) (75)

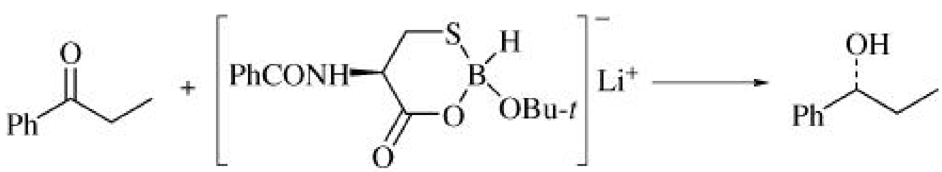
*3.3.1.1. Synthesis of Reagent **43***

All operations were performed under a N_2 atmosphere. To a slurry of 9-BBN, (**41**) (32.3 g, 265 mmol) suspended in THF (200 mL) was added a solution (330 mL) of 1,2:5,6-di-*O*-isopropylidene- α -d-glucofuranose, (**38**) (69 g, 265 mmol) in THF dropwise via a double-ended needle with vigorous stirring. Evolution of hydrogen ceased within 1 hour, and the mixture was stirred for an additional 2 hours. Evaporation of solvent, followed by distillation of the residue under vacuum, yielded highly viscous 9-*O*-(1,2:5,6-di-*O*-isopropylidene- α -d-glucofuranosyl)-9-borabicyclo[3.3.1]nonane, (**42**) (89 g, 88% yield): bp 198–201°/0.5 torr; ^{11}B NMR δ 56.30 (s); MS, M^+ 380. An oil suspension of potassium hydride, transferred to a flask, was allowed to settle and most of the oil decanted with a double-ended needle. Then the potassium hydride was washed with pentane (3 × 100 mL). To this oil-free potassium hydride (12 g, 300 mmol) suspended in THF (150 mL) was added a THF solution (250 mL) of **42** (76 g, 200 mmol) slowly via a double-ended needle with vigorous stirring. The reaction became slightly exothermic after a 10–30 minute induction period. The reaction can be monitored both by hydrolysis of centrifuged aliquots and by ^{11}B NMR. It was complete within 2 hours, producing a solution of the addition compound, potassium 9-*O*-(1,2:5,6-di-*O*-isopropylidene- α -d-glucofuranosyl)-9-borabicyclo[3.3.1]nonane (**43**) (0.48 M, 96% yield): ^{11}B NMR δ 1.33 (br s): IR 2038 cm^{-1} (s). Hydride and potassium were determined as hydrogen and KOH following hydrolysis; boron was estimated as

1,5-cyclooctanediol following oxidation by alkaline hydrogen peroxide: [H] = 0.48 M; [K] = 0.48 M; [B] = 0.50 M.

3.3.1.2. Enantioselective Reduction of Methyl 3,3-dimethyl-2-oxobutanoate with ***43***

An oven-dried, 50-mL long-necked round-bottomed flask equipped with a septum-capped side arm, magnetic stirring bar, and stopcock adaptor connected to a mercury bubbler was assembled while hot and flushed with a stream of nitrogen. The flask was charged with the THF solution of reagent **43** (0.43 M, 26 mL, 11 mmol) and cooled to –78°. To the flask was added a solution of 1.44 g of methyl 3,3-dimethyl-2-oxobutanoate (10 mmol) in 7 mL of THF precooled to –78° via a double-ended needle. After the reaction mixture was stirred, it was maintained at –78° for 10 hours. The excess hydride was then destroyed by addition of 2 mL of methanol precooled to –78°. After the volatiles were removed at aspirator pressure, the residue was dissolved in 25 mL of diethyl ether. The mixture was cooled to 0° and oxidized with 3 mL of 30% hydrogen peroxide in 4 mL of pH 7 phosphate buffer solution at 0° for 3 hours. The ether layer was separated and the aqueous layer was extracted with 3 × 25-mL portions of diethyl ether. The combined extract was washed once with saturated brine solution (15 mL), dried over anhydrous magnesium sulfate, and filtered. The filtrate was concentrated. Distillation of the residue provided 1.11 g of methyl 3,3-dimethyl-2-hydroxybutanoate (76%, bp 77–80°/18 mm Hg) containing a small amount of impurities. The alcohol was further purified by preparative GC (20 % Carbowax 20 M, 6ft × 1/2 in. column, 100°) and the rotation was measured: $[\alpha]^{22}_{D}$ + 40.4° (*c* 3.22, $CHCl_3$), maximum reported rotation $[\alpha]^{20}_{D}$ – 35.8° (*c* 3.16, $CHCl_3$). Capillary GC analysis (Supelcowax, 15 M) of MTPA esters of the product alcohol revealed a composition of 98.5% *S* + 1.5% *R* (i.e., 97% ee).



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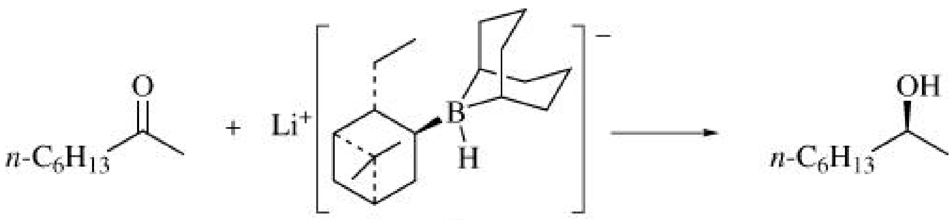
3.3.2. Enantioselective Reduction of Propiophenone with (R)-N-Benzoylcysteine $LiBH_4$ Reagent (37) (54)

A THF solution of $LiBH_4$ (3.6 mmol) was added to a solution of (*R*)-*N*-benzoylcysteine **(35)** (2.4 mmol) and *t*-BuOH (1.6 mmol) in THF (8.5 mL) at room temperature under an argon atmosphere. After the mixture was heated at reflux for 30 minutes, it was cooled to –78° and a solution of propiophenone (0.134 g, 1 mmol) in THF (2 mL) was added. The mixture was stirred for 4.5 hours while the temperature was allowed to warm from – 78 to –40°. The reaction was quenched by adding 1 M HCl (3 mL). Aqueous $NaHCO_3$ (5%) was added until the pH of the mixture became about 10. The mixture then was extracted with ether, and the organic layer was washed with 5% $NaHCO_3$ solution. The extract was dried over anhydrous sodium sulfate and then evaporated on a rotary evaporator. The residue was purified on silica gel TLC (chloroform as developing solvent) to produce (*R*)-(+)-1-phenyl-1-propanol (96 mg, 71%) as a colorless oil. After bulb-to-bulb distillation (bp 107°/15 mm Hg), the optical rotation was observed: $[\alpha]^{20}_D$ + 41.4° (*c* 5.09, $CHCl_3$); 91.2% ee based on the maximum rotation reported. Enantiomeric excess (85.5 ± 2.5% ee) was determined by ^1H NMR analysis of (+)- α -methoxy- α -trifluoromethylphenylacetic acid (MTPA) ester derivatives. Recovery of **35** was performed by extraction of aqueous washings with ethyl acetate after acidification (85% yield).



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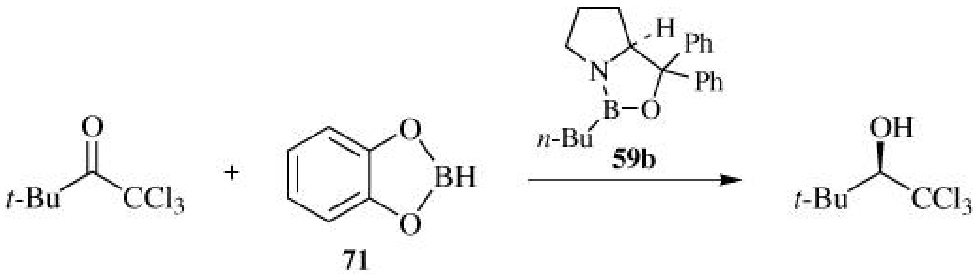
3.3.3. Enantioselective Reduction of 2-Octanone with Lithium B-Iso-2-ethylapopinocampheyl-9-borabicyclo[3.3.1]nonyl Hydride (Eapine-Hydride, (46) (81)

Solid 9-BBN (**41**) (1.25 g, 10 mmol) was transferred under nitrogen to a 100-mL round-bottomed flask using a glove bag. 2-Ethylapopinene ($[\alpha]^{23}_D$ – 45.6° (neat), (>99% ee)) (1.65 g, 11 mmol) was syringed into the flask which was heated for 6 hours to form *B*-iso-2-ethylapopinocampheyl-9-borabicyclo-[3.3.1]nonane. This reagent was dissolved in THF (10 mL) and cooled to –78°. *tert*-Butyllithium (6.5 mL of 1.7 M in hexanes, 11 mmol) was added dropwise, and the reaction was stirred at –78° for 2 hours and then warmed to 25° to form Eapine-Hydride (**46**) (^{11}B NMR: δ – 6.2 ppm, d, *J* = 80 Hz). The reagent was standardized by hydride estimation. (264)

A 5-m mol aliquot of this reagent was diluted with 5 mL of THF and 5 mL of ether and cooled to –100° (petroleum ether (30–60°)/2-propanol/acetone (4:1:1)/liquid nitrogen bath). A solution of 2-octanone (0.7 mL, 4.5 mmol) in 10 mL of THF/pentane/ether 4:1:1 was cooled to –100° in another flask and added dropwise to the reagent at –100° with a double-ended needle. The reaction was stirred for 3 hours and quenched with cold (–100°) ethanol (1 mL) and subjected to the usual alkaline H_2O_2 workup. (265) Extraction of the product in ether and distillation provided 0.47 g (80% yield) of 2-octanol. Analysis of the MTPA ester using an SPB-5 (30-m) capillary column showed a composition of 88.5% *S* isomer and 11.5% *R* isomer, i.e., an ee of 77%.



(159)

3.4. Enantioselective Reduction of 3,3-Dimethyl-1,1,1-trichloro-2-butanone with an oxazaborolidine Catalyst (115)

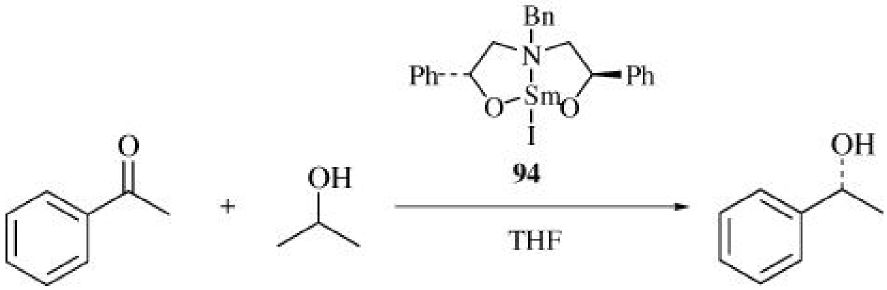
3.4.1.1. (S)- α , α -Diphenyl-2-pyrrolidinemethanol (57)

A 5-L three-necked flask fitted with a mechanical stirrer, nitrogen inlet tube, 2-L addition funnel containing a THF solution of (*S*)-tetrahydro-1*H*,3*H*-pyrrolo[1,2-*c*]oxazole-1,3-dione (61), (*S*)-Pro-NCA, and a Teflon-coated thermocouple probe was charged with a solution of phenylmagnesium chloride in THF (2.0 M, 1.5 g/L, 3.0 mol). The Grignard reagent was cooled to –15°. The THF solution of (*S*)-Pro-NCA (ca. 0.95–1.0 mol) was added over 1 hour while maintaining the internal temperature at – 10 to –15°. After the addition was complete, the mixture was aged for 3 hours at –15° and for 1 hour at 0°. The reaction was quenched into a 12-L mechanically stirred flask containing a precooled (0°) solution of 2 M aqueous H_2SO_4 (2.0 g/L, 4.0 mol), over 0.5–1.0 hour, maintaining the internal temperature below 20°. During the quench, a thick white precipitate of $MgSO_4$ formed. The mixture was agitated for 1 hour at 0° and filtered through a 3-L, medium-frit, sintered-glass funnel. The $MgSO_4$ cake was washed free of residual product with THF (3 × 1 g/L). The filtrate and THF washes were combined and concentrated at atmospheric pressure to a volume of 2 g/L. *Caution: benzene (ca. 82 g), formed during the quench of excess PhMgCl, is removed during the concentration* . The product as its sulfate salt, Ph_2CO, and Ph_3COH precipitate during the concentration. The mixture was cooled to 0–5°, aged for 1 hour, and filtered. The cake was (3 × 350 mL) to remove the Ph_2CO and Ph_3COH. The cake was dried in vacuo (40°, 50 mbar), affording 221 g (73% from proline) of (*S*)- α , α -diphenyl-2-pyrrolidinemethanol sulfate as a white solid: mp 275–290° (dec). Anal. Calcd for $C_{34}H_{40}N_2O_6S$: C, 67.52; H, 6.67; N, 4.63. Found: C, 67.75; H, 6.67; N, 4.51.

A portion of the sulfate salt was converted to the free base as follows: To a mechanically stirred solution of THF (50 mL) and 2 M aqueous NaOH (50 mL, 100 mmol) at 20° was added the sulfate (15.1 g, 25.0 mmol). The mixture was stirred at 20° until all solids dissolved and was then diluted with toluene (200 mL). The two-phase mixture was filtered through a medium-frit sintered glass funnel and partitioned, and the organic layer was washed with H_2O (25 mL). The organic layer was concentrated in vacuo (50°, 1 mbar), affording 12.5 g (99% yield) of (*S*)- α ,α-diphenyl-2-pyrrolidinemethanol (**57**) as a colorless oil that crystallized on standing. An analytical sample was prepared by recrystallization from hexane: mp 79–79.5°; IR (CCl_4) 3600–3300 (br), 3160, 3140, 2980, 2790, 1490, 1450, 1400, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7–7.5 (m, 4 H, Ar-H), 7.4–7.1 (m, 6 H, Ar-H), 4.65 (s, 1 H, OH), 4.3 (t, *J* = 7.4 Hz, 1 H, C2-H), 3.1–2.9 (m, 2 H, C5-H), 1.9–1.5 (m, 5 H, C3-H, C4-H, NH); ^{13}C NMR ($CDCl_3$) δ 148.21, 145.41, (C1′,C1²), 128.24, 127.98 (C3′,C3²,C5′,C5²), 126.46, 126.36 (C4′,C4²), 125.88, 125. 55 (C2′,C2²,C6′,C6²), 77.1 (C α), 64.41 (C2), 46.68 (C5), 26.30 (C3), 25.51 (C4); GC/MS $[M + H]^+$ at *m/z* 254.1; $[\alpha]21_{589}$ – 54.3° (*c* 0.261, MeOH). Anal. Calcd for $C_{17}H_{19}NO$: C, 80.60; H, 7.50; N, 5.53. Found: C, 80.80; H, 7.64; N, 5.49.

3.4.1.2. Enantioselective Reduction of 3,3-Dimethyl-1,1,1-trichloro-2-butanone with oxazaborolidine Catalyst

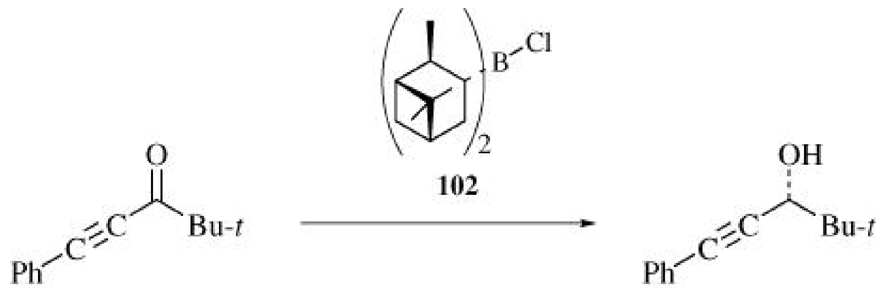
(*S*)- α , α -Diphenyl-2-pyrrolidinemethanol (**57**) (835 mg, 3.3 mmol), *n*-butylboronic acid (404 mg, 4.0 mmol), and 20 mL of toluene were heated at reflux in a Dean-Stark apparatus containing 3 Å molecular sieves in the side arm under nitrogen for 12 hours. Concentration to ca. 3 mL at 1 atm, removal of the remaining toluene in vacuo, and addition of 15 mL of dry, air-free toluene afforded a 0.2 M solution of (*S*)-oxazaborolidine catalyst. Addition of 3,3-dimethyl-1,1,1-trichloro-2-butanone (6.75 g, 33 mmol), cooling to –78°, and dropwise addition of a toluene solution of catecholborane (15 mL, 49.5 mmol) over 10 minutes with vigorous stirring afforded a white precipitate. The mixture was warmed to –20° to effect solution, and after 56 hours at –20°, the reaction was quenched with methanolic HCl (744 μ L, 0.5 M) and concentrated at 20 Torr. Addition of 40 mL of 2:1 low-boiling petroleum ether-ether afforded (*S*)- α , α -diphenylprolinol·HCl (875 mg, 92%), which was recovered by filtration. The filtrate was diluted with 90 mL of ether, washed with saturated aqueous Na_2CO_3 until colorless (7 × 30 mL) and then brine (3 × 30 mL), dried ($MgSO_4$), and concentrated to afford (*R*)-3,3-dimethyl-1,1,1-trichloro-2-butanol as a volatile colorless solid (7.63 g, containing 15 mass % toluene by ^1H NMR, 96% corrected yield, 97% ee); similar reduction of 633 mg of ketone afforded the alcohol in 96% yield and > 99% ee. An analytical sample was prepared by chromatography on silica gel with 15:1 low-boiling petroleum ether-ether: mp 45–47°; $[\alpha]^{24}_D$ – 9.33° (*c* 1.65, $CHCl_3$); ^1H NMR (270 MHz, $CDCl_3$) δ 3.91 (d, 1 H, *J* = 5.5 Hz), 2.95 (d, 1 H, *J* = 5.5 Hz, OH), 1.22 (s, 9 H); IR (neat) 3500, 2990–2930 cm^{-1}; CIMS (triethylsilylether) 336 (M + NH^4) + ; HRMS (triethylsilyl ether) calcd for $C_{12}H_{24}Cl_3OSi$ + NH_4) + 336.1084, found 336.1057.



(160)

3.4.2. Enantioselective Meerwein-Ponndorf-Verley Reduction of a Ketone with a Chiral Samarium-based Catalyst (146)

Under an argon or nitrogen atmosphere, 36 mg (0.1 mmol) of enantiopure amino alcohol ligand **93** (266, 267) in 0.5 mL of THF was cooled to 0° and deprotonated with 1.9 equiv of *n*-BuLi. The use of hydroxide-contaminated *n*-BuLi was deleterious to both enantioselectivity and reaction rate. The ligand solution was warmed to room temperature and transferred via cannula into a second flask containing a slurry of SmI_3 prepared by oxidation of SmI_2 (0.1 mmol) with 15 mg (0.053 mmol) of diiodoethane. After transfer of the residual ligand into the reaction flask with an additional 0.4 mL of THF, the homogeneous orange catalyst solution was stirred for 1 hour at ambient temperature. To the catalyst solution was added 3.8 mL of 2-propanol (50 mmol) followed by 2 mmol of acetophenone (final 2-propanol: THF ratio = 2:1). After 24 hours, the reaction was quenched by addition of a saturated aqueous solution of potassium sodium tartrate, and the resulting slurry was concentrated. The oil thus obtained was diluted with 1 M aqueous HCl and extracted with ethyl acetate. The organic extracts were concentrated and the resulting slurry was diluted with ether, allowing the insoluble HCl salt of the chiral ligand to be collected by filtration. The ethereal layer was dried over $MgSO_4$ and concentrated in vacuo. Flash chromatography afforded (*R*)-1-phenylethanol in 74% isolated yield and in 96% ee [determined by chiral GLC assay (Chiraldex G-TA)].



(161)

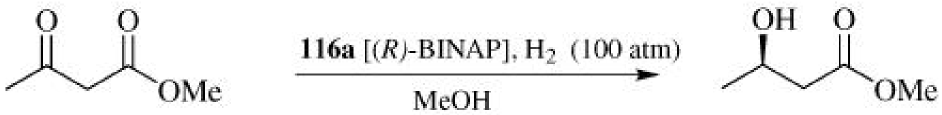
3.4.3. Enantioselective Reduction of Acetylenic Ketones with B-Chlorodiisopinocampheylborane (DIP-Cl, 102) (268)

An oven-dried, 50-mL round-bottomed flask equipped with a side arm, magnetic stirring bar, and a connecting tube was cooled to room temperature in a stream of nitrogen. *B*-Chlorodiisopinocampheylborane (**102**) (3.52 g, 11.0 mmol) was transferred to the flask in a glove bag and dissolved in ether (10 mL). The solution was cooled to –25°, and the ketone (10 mmol) was added. The reaction was followed by ^{11}B NMR spectrometry after aliquots were methanolyzed at –25° at periodic intervals. When the reaction was complete (^{11}B, δ 32 ppm), the mixture was warmed to 0° and acetaldehyde (0.73 mL, 13 mmol) was added dropwise (exothermic reaction!). The mixture was warmed to room temperature and stirred for 3 hours. When the ^{11}B NMR spectrum showed a singlet at δ 18 ppm, sodium hydroxide (6 N, 10 mL) was added to the mixture and the organics were extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and distilled to separate the α -pinene and the product alcohol. The alcohol was further purified by preparative GC with appropriate columns (SE-30 or Carbowax 20 M).

3.4.3.1. 4,4-Dimethyl-1-phenyl-1-pentyn-3-ol

Following the general procedure, 4,4-dimethyl-1-phenyl-1-pentyn-3-one (10 mmol) was treated with 11 mmol of **102** in ether at –25°. The reaction was very slow and required 6 days for completion. Workup provided 4,4-dimethyl-1-phenyl-1-pentyn-3-ol in 75% yield: bp 121–122°/0.35 mmHg. Analysis of the MTPA esters on an SPB-5 capillary column showed only a single peak on the chromatogram corresponding to only one isomer present, i.e., > 99% ee.

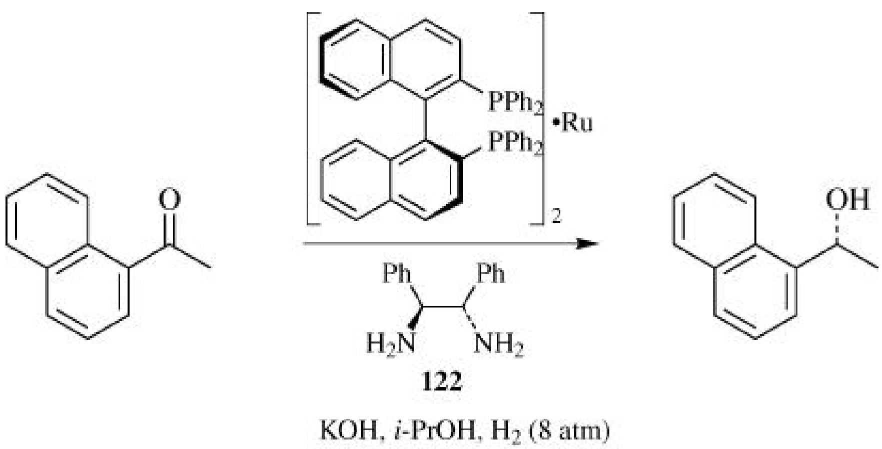
When this reaction was repeated without solvent at room temperature it was complete in 8 hours. The product alcohol was isolated in 79% yield: bp 122°/0.35 mm Hg; $[\alpha]^{23.9}_{D}$ 2.14 (*c* 5.0, $CHCl_3$). Analysis of the MTPA ester showed an ee of 98%: IR (neat) 3358 (OH), 2200 (C ≡ C); ^{1}H NMR δ ($CDCl_3$) 1.05 (s, 9 H, $(CH_3)_3$), 2.3 (br s, 1 H, OH) 4.25 (s, 1 H, CHOH), 7.2 (m, 3 H, Ph), 7.4 (m, 2 H, Ph); ^{13}C NMR δ ($CDCl_3$) 25.40 (C_5), 36.11 (C_4), 71.78 (C_3), 85.65 (C_1), 89.06 (C_2), 122.83 ($C_{1¢}$), 128.26, 131.67; MS EI *m/z* 188 M^+, 173 $(M - CH_3)^+$, 131 $(M - CMe_3)^+$ (100).



(162)

3.4.4. Enantioselective Hydrogenation of Methyl 3-Oxobutanoate with BINAP-Ru Complex

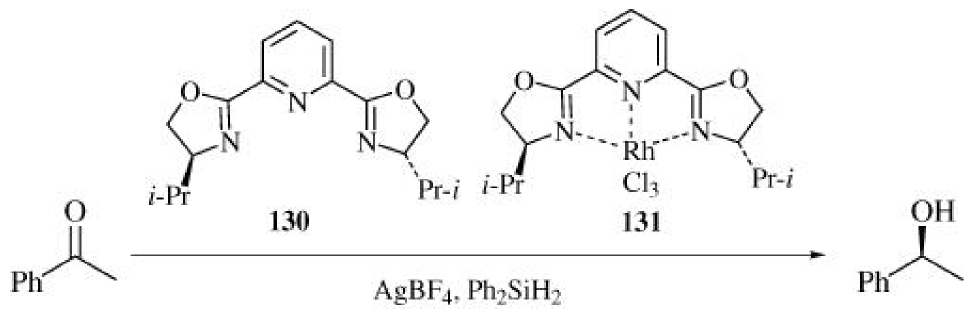
For complete experimental details see *Organic Syntheses* **1992**, *71*, 1–13.



(163)

3.4.5. Enantioselective Hydrogenation of an Aromatic Ketone Catalyzed by a BINAP-Ru(II) Complex-Chiral Diamine-KOH System (196)

(*S,S*)-1,2-Diphenylethylenediamine (**122**) (7.5 mg, 0.035 mmol) and a 0.5 M 2-propanol solution of KOH (140 μ L, 0.070 mmol) were added to 2-propanol (10 mL) and the mixture was degassed by freeze-thaw cycles. To this solution was added $RuCl_2$[(*S*)-BINAP]$(dmf)_n$ (269) (33.1 mg, 0.035 mmol), and the resulting mixture was sonicated for 10 minutes and used as a catalyst. A solution of 1¢-acetonaphthone (30.0 g, 176 mmol) in 2-propanol (90 mL) was subjected to freeze-thaw cycles. These two solutions were transferred to a glass autoclave, hydrogen was pressurized to 8 atm, and the solution was vigorously stirred at 28° for 24 hours. After venting hydrogen, the solvent was removed under reduced pressure, and the residue was distilled to give (*R*)-1-(1-naphthyl)ethanol (27.90 g, 92% yield, 95% ee), bp 98–100°/0.5 mmHg, $[\alpha]^{25}_D$ + 75.8° (*c* 0.99, ether) (lit. (270) $[\alpha]^{25}_D$ + 82.1° (*c* 1.0, ether)). The yield determined by ^{1}H NMR was > 99%.

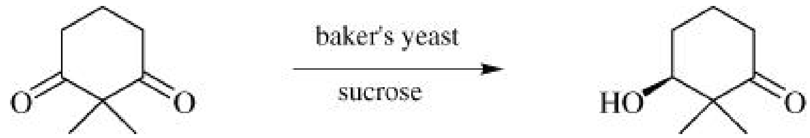


(164)

3.4.6. Hydrosilylation of a Ketone with a Rhodium Complex and Diphenylsilane (210)

In a 20-mL flask was placed **130** (0.32 mmol, 4 mol %), **131** (0.08 mmol, 1 mol %), and silver fluoroborate (0.16 mmol) under a nitrogen atmosphere. Anhydrous THF (1.0 mL) was added, and then the mixture was magnetically stirred at room temperature for 1 hour. After addition of acetophenone (8.0 mmol), the reaction flask was dipped in a thermoregulated bath of methanol-water at –10°. Diphenylsilane (2.36 g, 12.8 mmol) was slowly added by a syringe. The temperature was gradually raised to –5° and then to 5°. The reaction was monitored by TLC: acetophenone (*Rf* 0.2), the corresponding silyl ether (*Rf* 0.6), diphenylsilane (*Rf* 0.7), and 1-phenylethanol (*Rf* 0.1), with hexane-ether (5:1) as an eluent. After completion, methanol (5 mL) was slowly added at 0°. After gas evolution ceased, the reaction mixture was poured into a solution of hydrochloric acid (1 N, 14 mL) at 0°. The reaction flask was washed with small amounts of methanol and ether, and the washings were also added to the acid solution. The mixture was stirred at 0° for 1 hour and extracted with ether (15 mL × 4). The extract was washed with brine (6 mL) and dried over anhydrous $MgSO_4$. The product yield (94%) was determined by GLC analysis with addition of 1-methylnaphthalene (0.50 mL, 3.52 mmol) as an internal standard.

The extract was concentrated under reduced pressure, and the residue was passed through a short column of silica gel (20 g, hexane-ether as an eluent). After Kugelrohr distillation of the product, the optical rotation was measured. A portion of the product (ca. 0.1 mmol) was converted to the corresponding MTPA ester with (*R*)-(+)-MTPA (35 mg, 0.15 mmol) and $SOCl_2$ for determination of the enantioselectivity by ^{1}H NMR spectroscopy: ^{1}H NMR of the MTPA ester of (*S*)-1-phenylethanol (CH_3O) δ 3.56 for *S* and 3.47 for *R*, the ratio 97:3; $[\alpha]_D$ – 48° (CH_2Cl_2).



(165)

3.4.7. Baker's Yeast Reduction of a Fluorinated β -Diketone

For experimental details see *Organic Syntheses* **1989**, *68*, 56.

4. Tabular Survey

Tables I–VIII are organized in the sequence used in the Scope and Limitations section. Literature coverage through 1995 is as exhaustive as possible, using both computer scanning services and hand searches. Entries in each table are arranged in order of increasing number of carbon atoms in the ketone.

The following abbreviations are used in the tables:

Ac	acetyl
BINAP	2,2′-bis(diphenylphosphino)-1,1′-binaphthyl
Bn	benzyl
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
DMPS	dimethylphenylsilyl
ee	enantiomeric excess
HMPA	hexamethylphosphoric triamide
LAH	lithium aluminum hydride
MOM	methoxymethyl
NBD	norbornadiene
Np	naphthyl
s/c	substrate/catalyst ratio
TBS	*tert*-butyldimethylsilyl
Tf	trifluoromethanesulfonyl (triflyl)
THP	tetrahydropyranyl
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl

Table . Structures of Modifiers that are Identified only by Number in the Tables

View PDF

Table I. Enantioselective Reduction of Ketones with Chirally Modified $LiAlH_4$

View PDF

Table II. Enantioselective Reduction of Ketones with Chirally Modified Metal Hydrides

View PDF

Table III. Enantioselective Reduction of Ketones with Chiral Oxazaborolidine Catalysts

View PDF

Table IV. Enantioselective Reduction of Ketones with MPV Reagents

View PDF

Table V. Enantioselective Hydrogenation of Ketones using Transition Metal Catalysts

View PDF

Table VI. Enantioselective Hydrosilylation of Ketones using Transition Metal Catalysts

View PDF

Table VII. Enantioselective Reduction of Ketones with Baker's Yeast and Related Microorganisms

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Table VIII. Enantioselective Reduction of Ketones with Chiral Dihydropyridine Reagents

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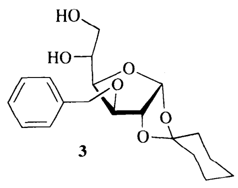
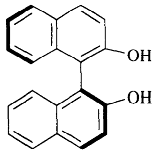
STRUCTURES OF MODIFIERS THAT ARE IDENTIFIED ONLY BY NUMBER IN THE TABLES

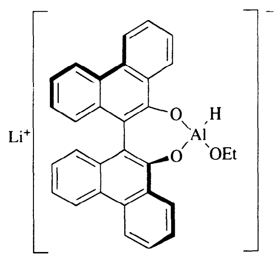
TABLE I



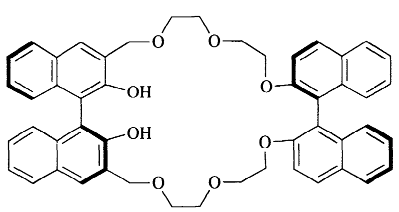
3



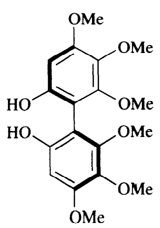
(*S*)-**5**



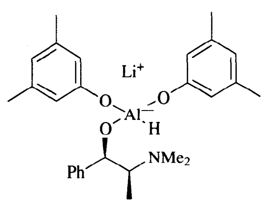
(*S*)-**9**



10

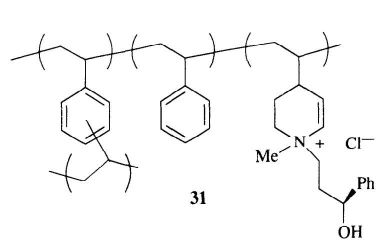


13

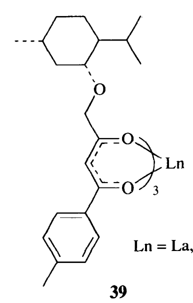


15 + 2 dimethylphenol = **16**

TABLE II



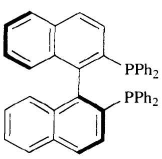
31



Ln = La, Pr, Gd, Er

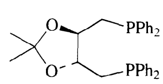
39

TABLE V

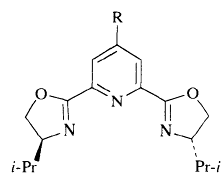


(*S*)-BINAP

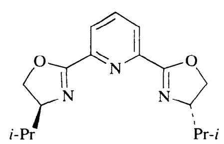
TABLE VI



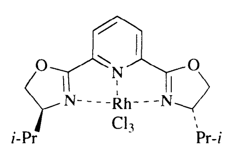
(*R,R*)-(—)-DIOP



132a; R = Me_2N
132b; R = MeO
132c; R = Cl



130 (PYBOX-R)



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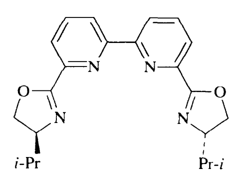

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TABLE VIII

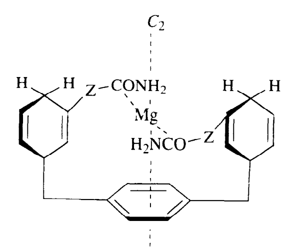

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TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$

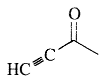
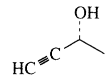
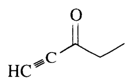
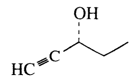
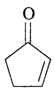
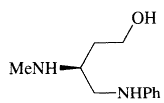
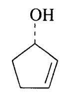
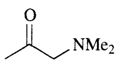
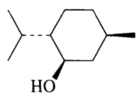
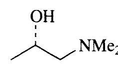
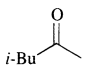
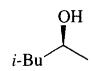
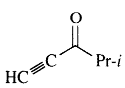
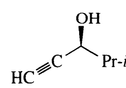
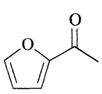
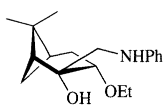
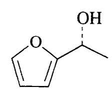
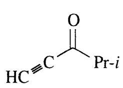
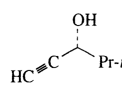
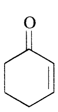
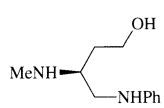
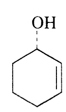
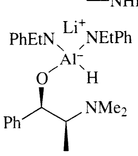
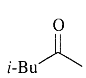
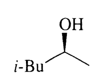
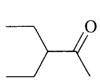
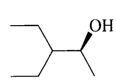
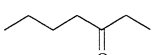
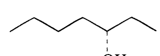
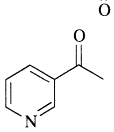
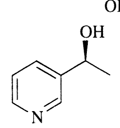
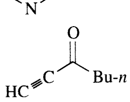
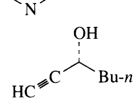
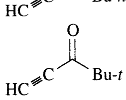
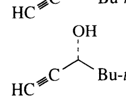
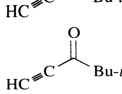
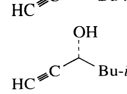
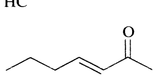
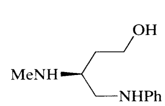
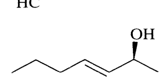
	Ketone	Chiral Modifier	Product(s), Yield(s) (%) and ee	Refs.
C_4		**16**	 (—) 79%	27
C_5		**16**	 (—) 86%	27
			 (77) 82%	38
			 (—) 87%	271
C_6		**9**	 (73) 21%	16
		(*S*)-**5**, MeOH	 (84) 57%	13
			 (88) 52%	41
		**16**	 (—) 86%	27
			 (95) 100%	38
			" (58) 32%	29
		**10**	 (78) 85%	17
C_7		**13**	 (54) 78%	21
		**13**	 (83) 36%	21
		**13**	 (53) 62%	21
		**16**	 (—) 85%	27
		**16**	 (—) 90%	27
		**16**	 (—) 88%	27
			 (73) 88%	38

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

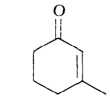
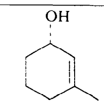
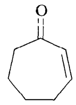
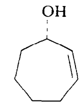
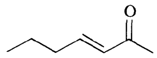
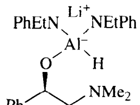
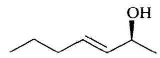
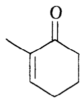
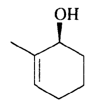
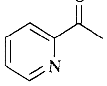
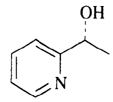
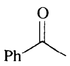
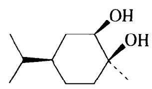
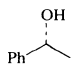
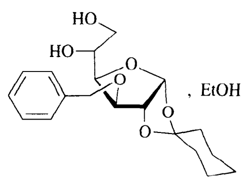
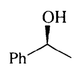
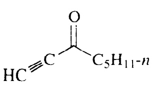
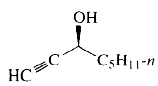
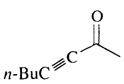
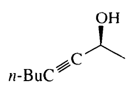
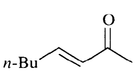
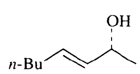
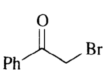
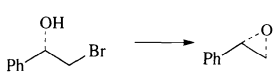
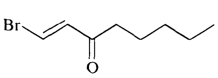
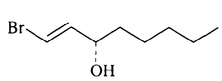
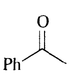
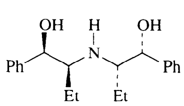
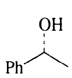
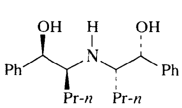
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
	"	 (57) 28%	38
	"	 (84) 50%	38
		 (92) 88%	29
	"	 (51) 58%	29
	"	 (—) 44%	271
C_8 	 , EtOH	 (99) 30%	9
	 , EtOH	" (—) 71%	272
	(*S*)-**5**, EtOH	 (61) 95%	12
	9	" (75) 97%	16
	(*S*)-**5**, MeOH	 (87) 84%	13
	(*R*)-**5**,MeOH	 (79) 84%	13
	(*R*)-**5**, EtOH	 (47) 79%	13
	(*R*)-**5**, EtOH	 (97) 95%	13
	(*S*)-**5**, EtOH	 (96) 96%	13
		 (98) 82%	40
		" (83) 79%	40

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

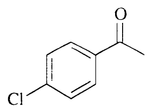
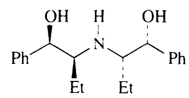
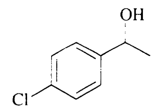
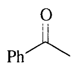
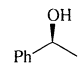
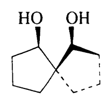
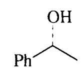
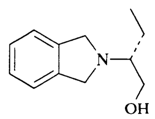
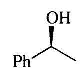
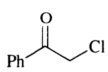
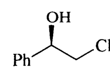
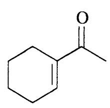
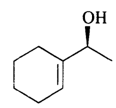
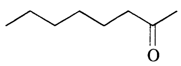
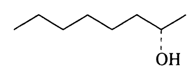
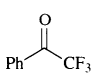
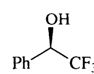
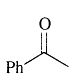
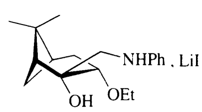
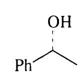
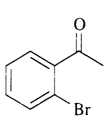
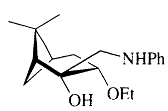
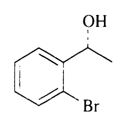
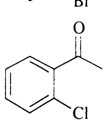
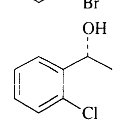
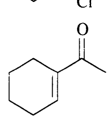
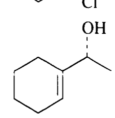
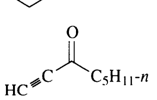
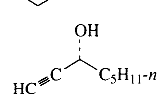
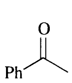
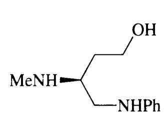
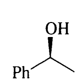
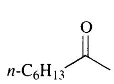
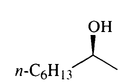
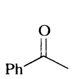
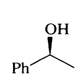
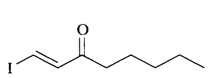
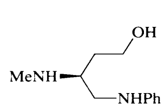
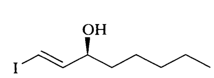
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
		 (95) 70%	40
	**10**	 (76) 89%	17
		 (80) 98%	20
		" (—) 63%	39
	13	 (93) 97%	21
	**13**	 (79) 86%	21
	**13**	 (68) 83%	21
	**13**	 (76) 76%	21
	(*S*)-**5**	 (97) 27%	273
		 (91) 83%	41
		 (86) 78%	41
	"	 (86) 78%	41
	"	 (89) 74%	41
	**16**	 (—) 84%	27
		 (87) 51%	37
	"	 (92) 33%	37
	**16**	 (90) 83%	25
		 (94) 51%	38

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ (*Continued*)

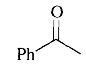
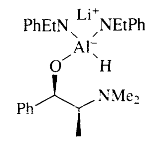
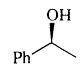
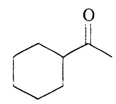
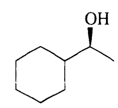
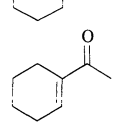
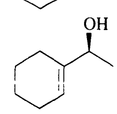
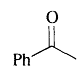
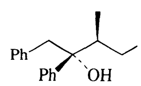
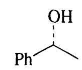
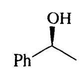
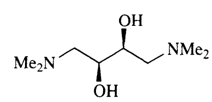
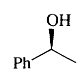
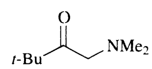
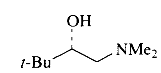
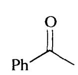
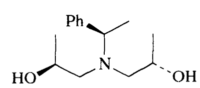
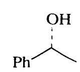
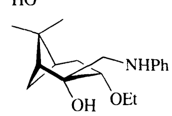
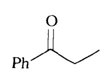
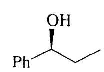
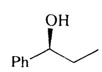
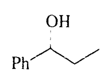
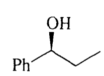
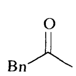
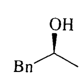
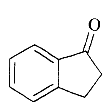
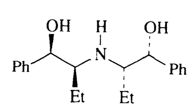
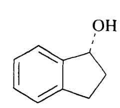
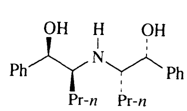
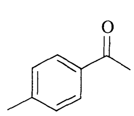
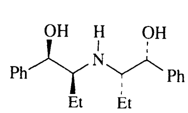
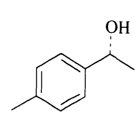
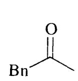
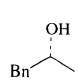
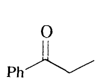
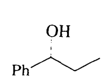
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
			(86)	88%	31
	"		(90)	35%	31
	"		(92)	78%	29
	 insoluble reagent		(100)	75%	274
	" soluble reagent		(77)	75%	274
			(—)	42%	275
	"		(—)	72%	271
			(98)	82%	276
		"	(85)	62%	41
C_9					
	**3**. EtOH		(—)	46%	272
	(*S*)-**5**. EtOH		(62)	98%	12
	3. EtOH		(—)	46%	272
	9		(78)	98%	16
	**9**		(76)	33%	16
			(96)	93%	40
		"	(83)	94%	40
			(79)	76%	40
	"		(85)	24%	40
	"		(87)	72%	40

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ (*Continued*)

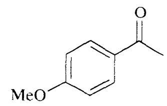
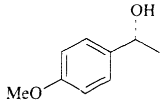
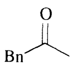
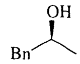
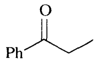
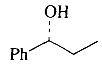
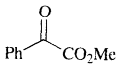
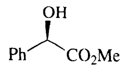
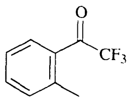
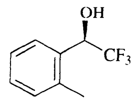
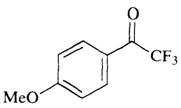
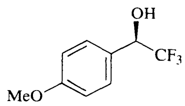
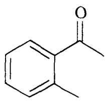
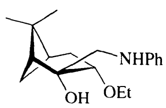
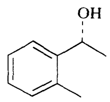
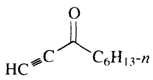
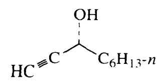
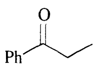
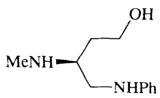
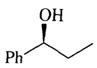
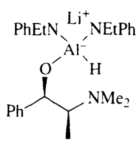
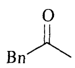
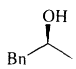
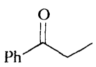
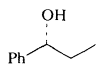
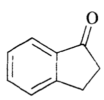
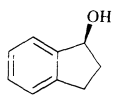
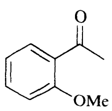
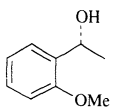
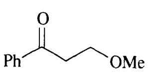
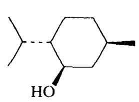
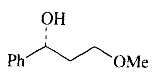
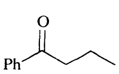
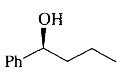
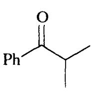
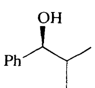
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
	"		(83)	86%	40
	"		(75)	88%	17
	"		(70)	90%	20
	"		(86)	81%	21
	(*S*)-**5**		(81)	74%	273
	(*S*)-**5**		(99)	6%	273
			(86)	79%	41
	**16**		(—)	83%	27
			(93)	68%	37
		"	(96)	90%	31
	"		(90)	41%	31
	"		(98)	77%	276
	"		(88)	71%	31
	"		(86)	91%	41
C_{10}					
			(—)	35%	8
	(*S*)-**5**, EtOH		(78)	100%	12
	(*S*)-**5**, EtOH		(68)	71%	12

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ (*Continued*)

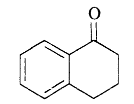
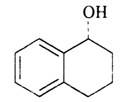
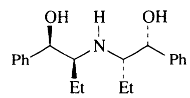
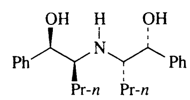
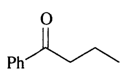
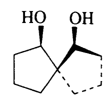
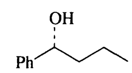
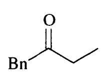
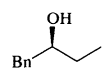
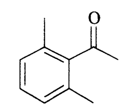
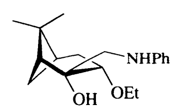
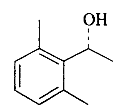
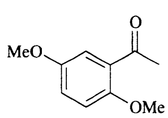
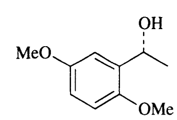
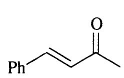
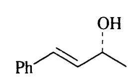
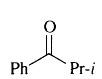
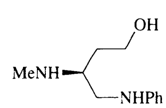
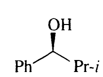
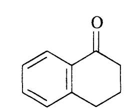
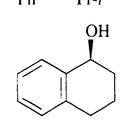
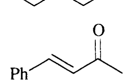
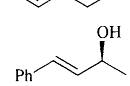
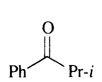
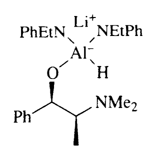
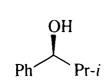
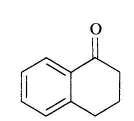
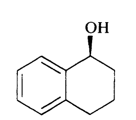
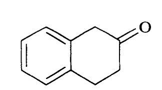
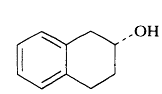
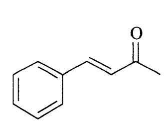
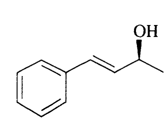
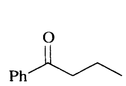
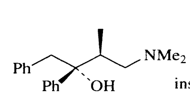
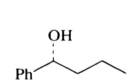
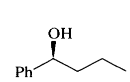
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
	(*R*)-**5**, EtOH		(91)	74%	13
		"	(98)	70%	40
		"	(88)	87%	40
			(65)	90%	20
	**13**		(72)	93%	21
			(87)	74%	41
	"		(91)	91%	41
	"		(93)	50%	41
	", LiI	"	(91)	52%	41
			(93)	77%	37
	"		(89)	88%	37
	"		(91)	72%	38
			(95)	78%	31
	"		(96)	51%	31
	"		(98)	67%	31
	"		(98)	98%	29
	 insoluble reagent		(100)	62%	274
	", soluble reagent		(50)	59%	274

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

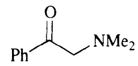
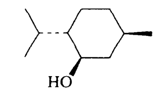
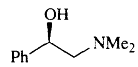
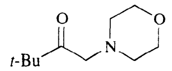
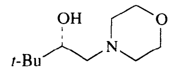
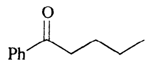
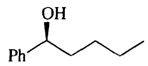
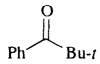
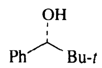
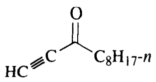
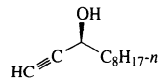
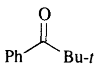
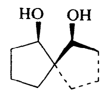
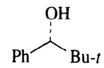
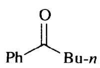
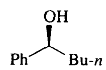
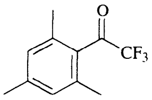
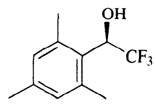
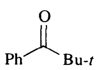
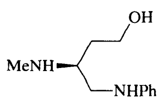
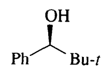
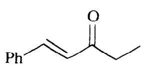
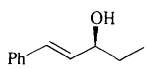
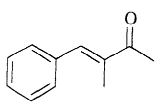
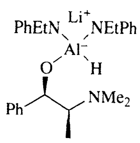
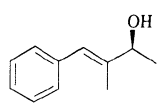
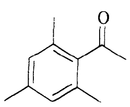
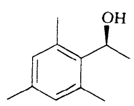
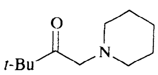
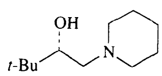
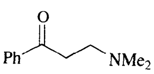
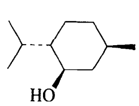
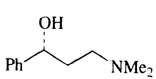
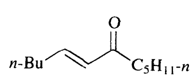
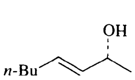
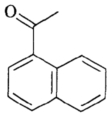
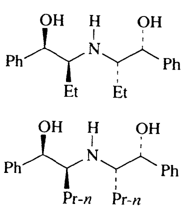
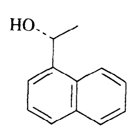
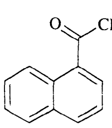
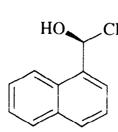
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
			(—)	58%	271
	"		(—)	31%	271
C_{11}					
	(*S*)-**5**, EtOH		(64)	100%	12
	(*R*)-**5**, EtOH		(80)	44%	13
	(*S*)-**5**, MeOH		(80)	96%	13
	(*S*)-**5**, EtOH	"	(74)	90%	13
			(69)	85%	20
	**13**		(84)	94%	21
	(*S*)-**5**		(69)	97%	273
			(84)	86%	37
	"		(95)	75%	38
			(100)	>90%	29
	"		(—)	75%	275
	"		(—)	34%	271
			(80-100)	78% 25%	7 8
C_{12}					
	(*R*)-**5**, EtOH		(91)	91%	13
			(95)	71%	40
		"	(90)	70%	40
	(*S*)-**5**		(93)	70%	273

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

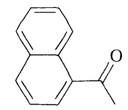
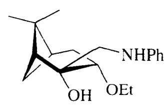
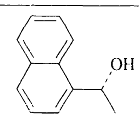
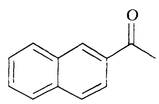
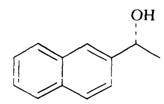
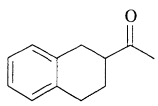
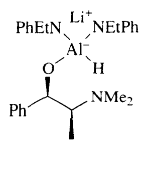
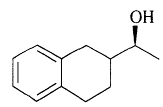
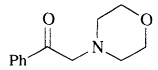
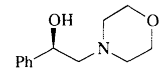
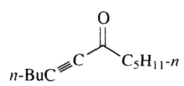
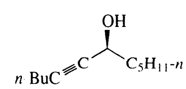
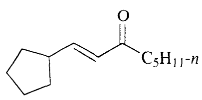
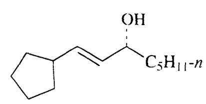
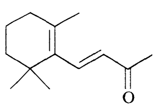
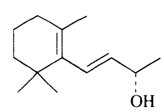
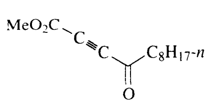
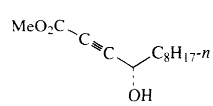
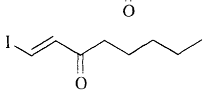
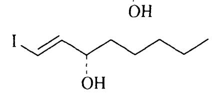
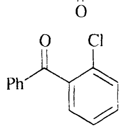
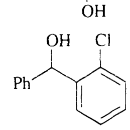
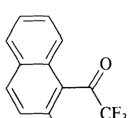
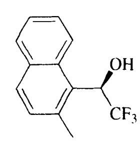
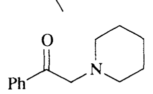
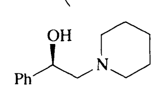
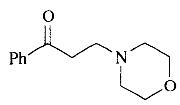
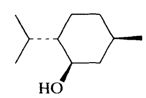
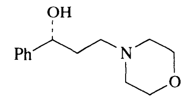
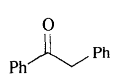
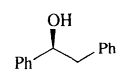
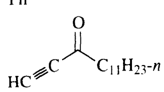
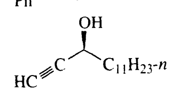
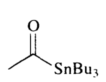
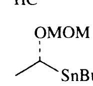
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
			(93)	80%	41
	", LiI	"	(92)	84%	41
	", HMPA	"	(85)	66%	41
	"		(96)	50%	41
			(100)	>90%	29
	"		(—)	95%	271
	(*S*)-**5**, MeOH		(85)	90%	13
C_{13}					
	(*R*)-**5**, EtOH		(91)	92%	13
	(*S*)-**5**, EtOH		(87)	100%	13
	(*S*)-**5**, MeOH		(80)	87%	13
	(*S*)-**5**, EtOH		(95)	97%	13
	(*S*)-**5**, EtOH		(—)	100%	39
	(*S*)-**5**, EtOH	"	(76)	76%	273
	(*S*)-**5**		(85)	93%	273
	(*S*)-**5**		(—)	29%	271
			(—)	59%	7
C_{14}					
	**9**		(77)	98%	7
	(*S*)-**5**, MeOH		(90)	92%	13
	(*S*)-**5**, MeOH; protect		(64)	91%	15
	(*S*)-**5**, EtOH; protect	"	(58)	94%	15

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

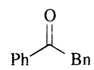
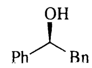
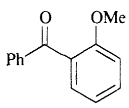
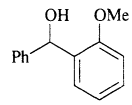
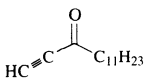
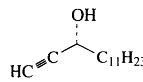
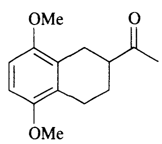
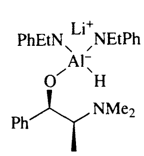
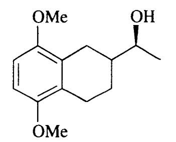
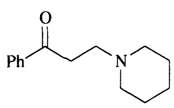
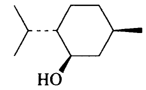
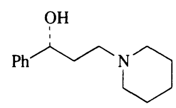
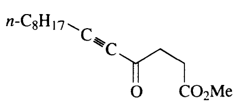
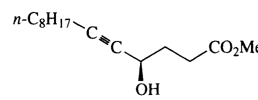
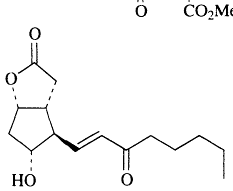
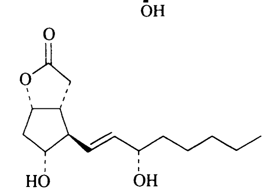
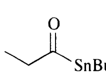
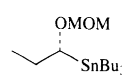
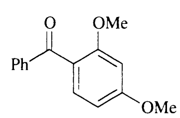
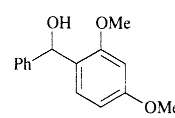
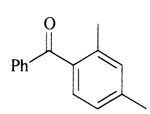
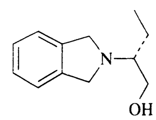
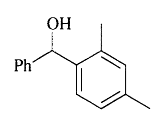
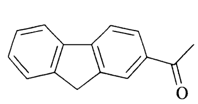
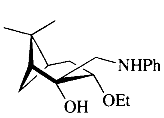
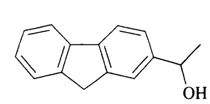
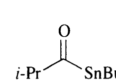
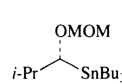
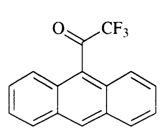
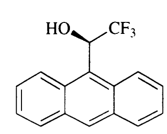
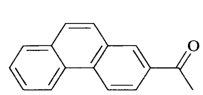
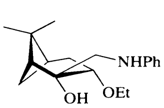
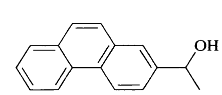
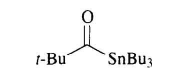
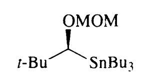
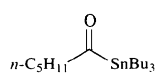
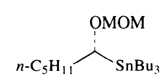
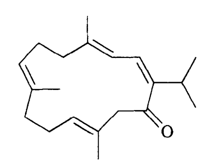
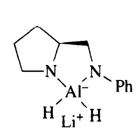
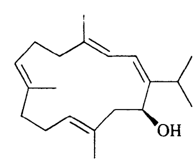
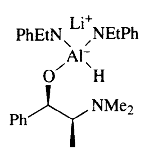
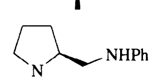
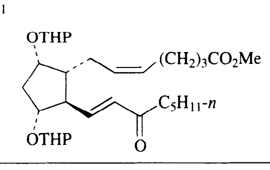
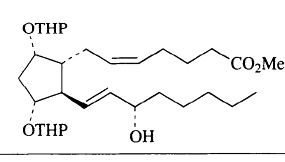
Ketone	Chiral Modifier	Product(s)	Yield(s) (%)	ee	Refs.
	(*S*)-**5**, *i*-PrOH	"	(54)	91%	15
	"		(77)	91%	17
	"		(—)	66%	39
	**16**		(—)	75%	27
			(94)	92%	29
			(80-100)	66% 37%	7 8
C_{15}					
	(*R*)-**5**, MeOH		(80)	84%	13
	(*S*)-**5**, EtOH		(97)	100% [a]	13
	(*S*)-**5**, MeOH; protect		(60)	90%	15
	(*S*)-**5**, EtOH; protect	"	(69)	96%	15
	(*S*)-**5**, EtOH		(—)	34%	39
			(—)	>95%	39
			(95)	81%	41
C_{16}					
	(*S*)-**5**, MeOH; protect		(—)	78%	15
	(*S*)-**5**, EtOH; protect	"	(52)	>96%	15
	(*S*)-**5**, *i*-PrOH; protect	"	(45)	80%	15
	(*S*)-**5**		(90)	98%	273
			(94)	87%	41

TABLE I. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED $LiAlH_4$ *(Continued)*

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
C_{17} 	(*S*)-**5**, *i*-PrOH; protect	 (55) 80%	15
C_{18} 	(*S*)-**5**, MeOH; protect	 (68) 90%	15
	(*S*)-**5**, EtOH; protect	" (52) 91%	15
	(*S*)-**5**, *i*-PrOH; protect	" (53) 92%	15
C_{20} 		 (88) 93%	45
		" (97) 87%	45
		" (78) 92%	45
C_{31} 	(*S*)-**5**, EtOH	 (88) 100% [a]	13

[a] This value was reported as "de".

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES

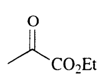
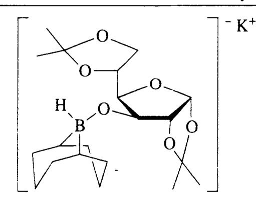
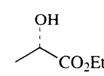
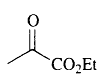
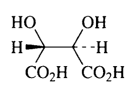
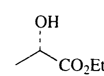
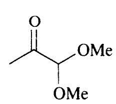
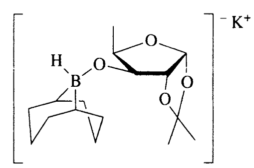
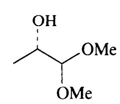
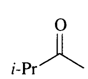
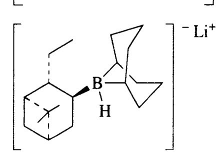
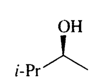
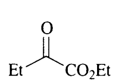
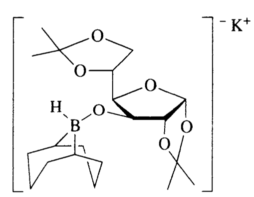
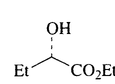
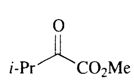
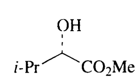
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee			Refs.
C_5					
			(75)	86%	75a
	 + $NaBH_4$		(36)	74%	51
			(70)	87%	78
			(—)	77%	81
C_6					
			(80)	92%	75a
	"		(83)	98%	75a

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

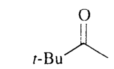
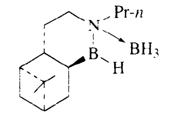
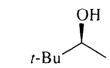
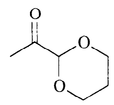
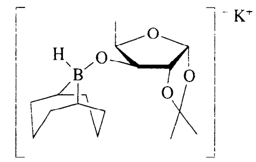
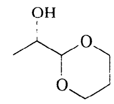
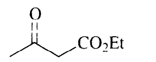
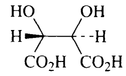
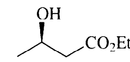
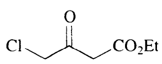
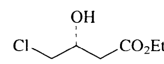
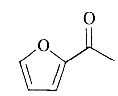
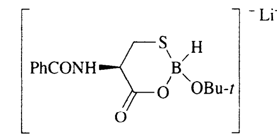
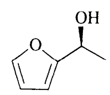
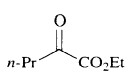
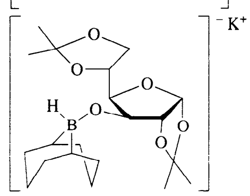
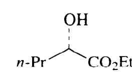
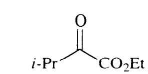
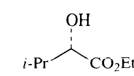
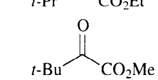
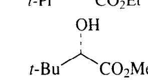
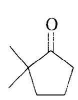
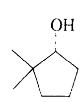
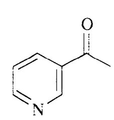
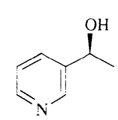
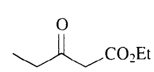
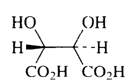
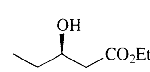
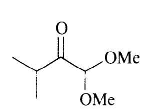
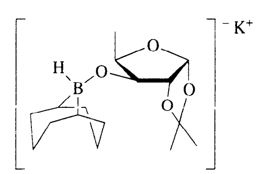
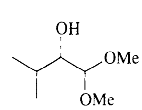
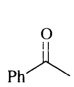
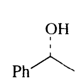
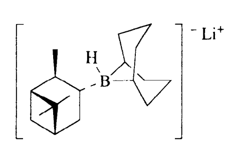
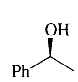
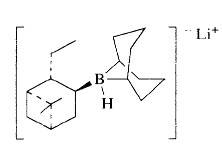
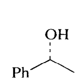
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee		Refs.
			(61) 82%	91
			(72) >99%	76
	 + $NaBH_4$		(65) 81%	51
	"		(81) 65%	51
			(82) 95%	63
C_7				
			(81) 94%	75a
	"		(85) 97%	75a
	"		(85) 97%	75a
	"		(—) 84%	75a
	"		(97) 70%	75a
	 + $NaBH_4$		(83) 75%	51
			(72) 90%	76
C_8 	"		(96) 70%	76
			(—) 20%	80
			(—) 61%	81

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

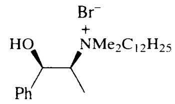
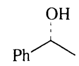
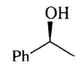
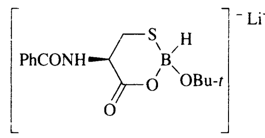
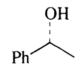
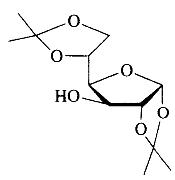
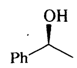
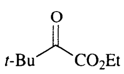
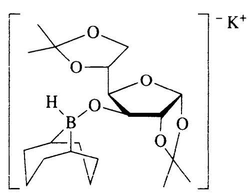
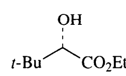
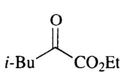
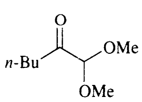
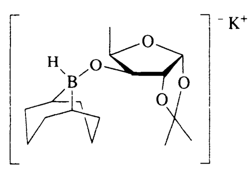
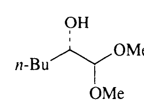
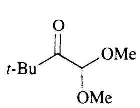
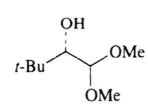
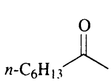
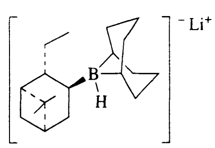
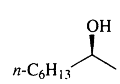
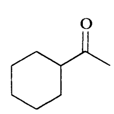
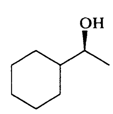
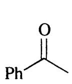
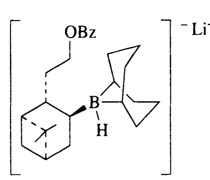
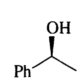
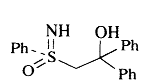
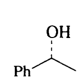
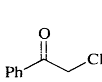
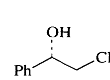
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee			Refs.
	 + $NaBH_4$		(—)	39%	47
	31 + $NaBH_4$		(71)	56%	49
			(66)	87%	54
	 + Me_2CHCO_2H + $NaBH_4$	"	(62)	78%	65
	" , $NaBH_4$, $ZnCl_2$		(100)	50%	72
	39 + $NaBH_4$	"	(64)	84%	69
			(87)	98%	75a
	"	"	(83)	93%	75a
			(80)	95%	76
	"		(76)	90%	76
			(85)	77%	81
	"		(—)	80%	81
			(80)	70%	82
	"	"	(80)	50%	82
	 + $NaBH_4$, TMSCl		(92)	84%	73
	" " "		(88)	88%	73

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

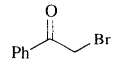
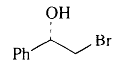
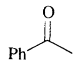
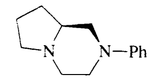
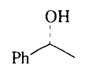
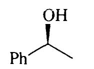
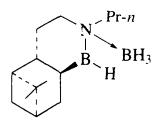
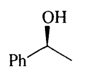
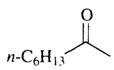
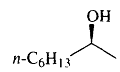
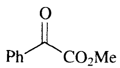
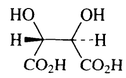
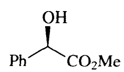
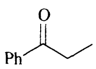
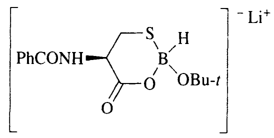
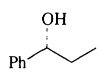
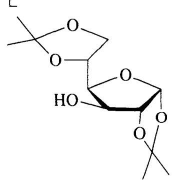
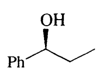
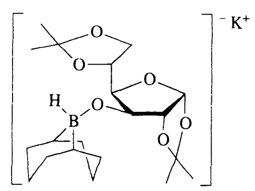
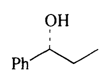
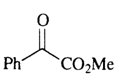
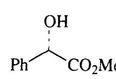
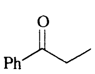
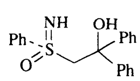
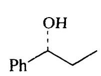
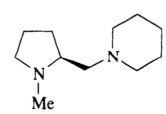
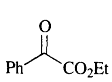
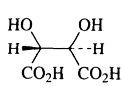
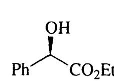
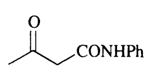
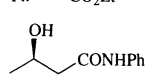
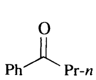
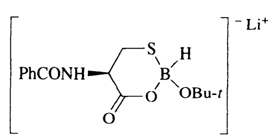
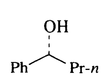
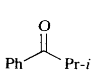
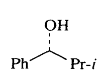
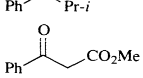
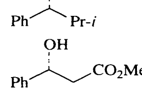
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee	Refs.
	" " "	 (80) 88%	73
	"	" (80) 88%	73
	 + $ZnCl_2$, $(i\text{-}Bu)_2AlH$, −100°, CH_2Cl_2	 (95) 97%	96
	β-cyclodextrin-pyridine-borane complex	 (8) 91%	277
		 (87) 77%	91
	"	 (76) 64%	91
C_9			
	 + $NaBH_4$	 (91) 71%	51
		 (54) 89%	54
	 + $NaBH_4$, $ZnCl_2$	 (100) 68%	69
		 (93) 92%	75a
	"	 (85) 92%	75a
	 + $NaBH_4$, TMSCl	 (86) 79%	73
	 + $ZnCl_2$, $Al(i\text{-}Bu)_2H$, CH_2Cl_2, −100°	" (98) 83%	96
C_{10}			
	 + $NaBH_4$	 (87) 86%	51
	"	 (83) 65%	51
		 (44) 92%	54
	"	 (60) 57%	54
	"	 (78) 84%	58

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

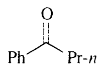
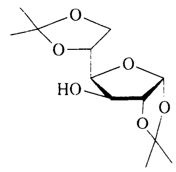
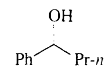
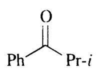
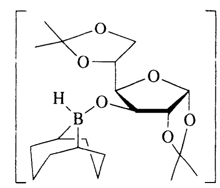
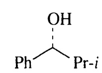
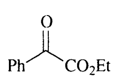
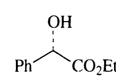
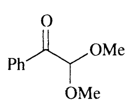
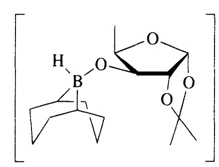
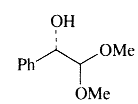
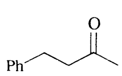
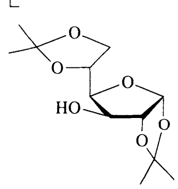
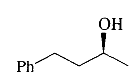
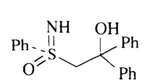
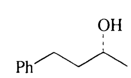
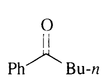
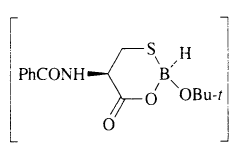
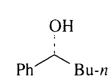
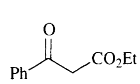
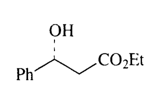
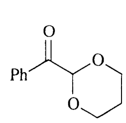
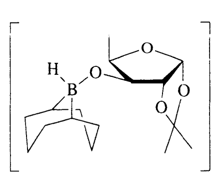
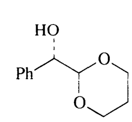
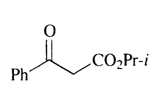
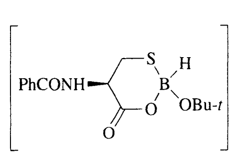
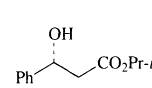
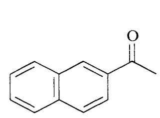
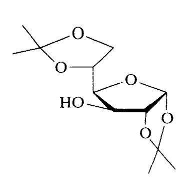
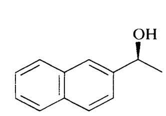
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee			Refs.
	 + Me_2CHCO_2H + $NaBH_4$		(53)	74%	65
	" + $NaBH_4$, $ZnCl_2$	"	(100)	58%	69
	 $^{-}$ K^+		(96)	87%	75a
	"		(80)	94%	75a
	 $^{-}$ K^+		(81)	92%	76
	 , benzene		(81)	62%	68
	 + $NaBH_4$, TMSCl		(82)	73%	73
	β-cyclodextrin-pyridine-borane complex	"	(26)	89%	277
C_{11} 	 $^{-}$ Li^+		(58)	88%	54
	"		(94)	87%	58
	 $^{-}$ K^+		(83)	96%	76
C_{12} 	 $^{-}$ Li^+		(83)	91%	58
	 + $NaBH_4$, $ZnCl_2$		(100)	68%	69

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

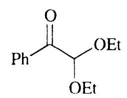
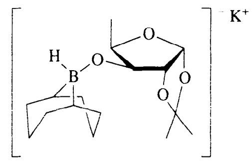
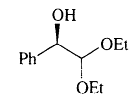
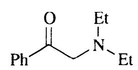
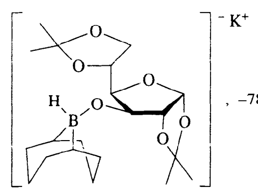
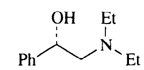
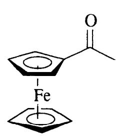
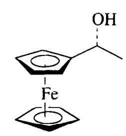
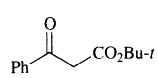
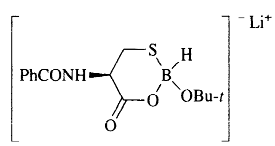
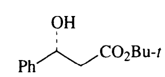
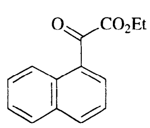
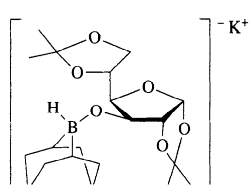
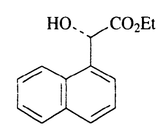
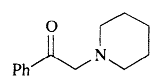
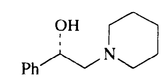
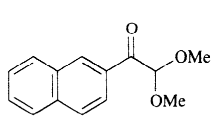
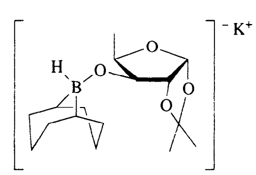
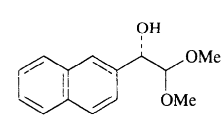
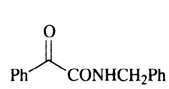
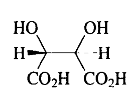
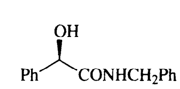
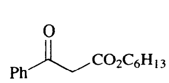
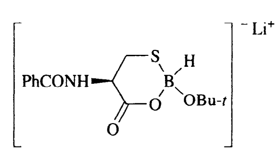
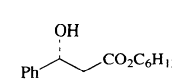
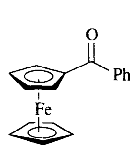
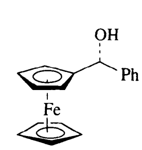
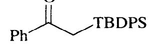
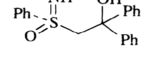
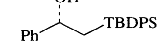
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee			Refs.
			(80)	93%	76
	 , −78°		(81)	73%	76
	β-cyclodextrin complex, $NaBH_4$, KCl		(59)	41%	85
C_{13}					
			(88)	90%	58
			(78)	96%	75a
	", −78°		(82)	60%	76
C_{14}					
			(87)	92%	76
C_{15}					
	 + $NaBH_4$		(100)	68%	51
			(66)	86%	58
C_{17}					
	β-cyclodextrin complex, $NaBH_4$, KCl		(55%)	84%	85
C_{24}					
	 + $NaBH_4$, TMSCl		(88)	90%	73

TABLE II. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALLY MODIFIED METAL HYDRIDES (*Continued*)

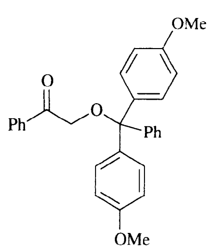
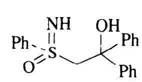
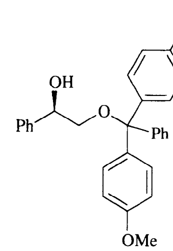
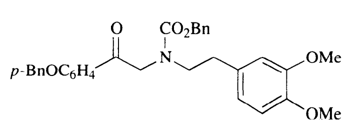
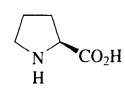
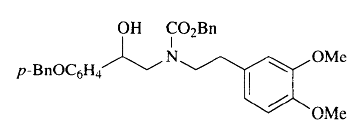
Ketone	Chiral Modified Borohydride	Product(s), Yield(s) (%), and ee	Refs.
C_{29}			
	 + $NaBH_4$, TMSCl	 (85) 87%	73
C_{33}			
	 + $NaBH_4$	 (—) 62%	53

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS

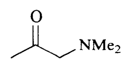
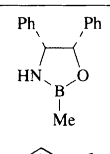
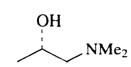
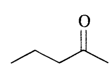
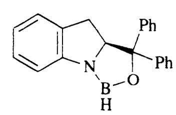
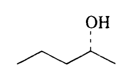
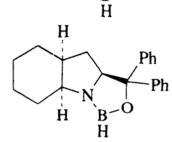
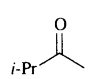
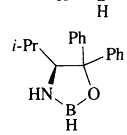
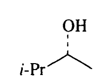
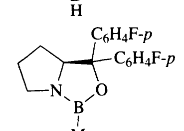
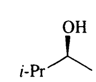
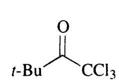
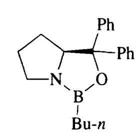
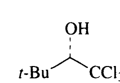
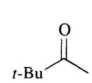
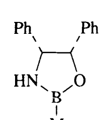
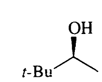
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee			Refs.
C_5					
			(—)	87%	277a, 278
			(92)	59%	279
		"	(90)	58%	279
			(100)	60%	100
			(—)	>99%	108
C_6					
	 , catecholborane, –20°		(—)	98%	127
			(—)	88%	277a, 278

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS *(Continued)*

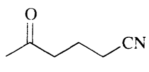
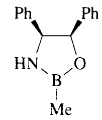
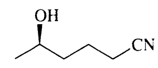
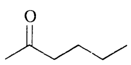
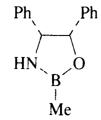
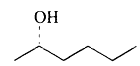
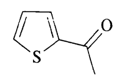
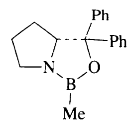
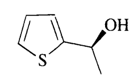
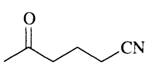
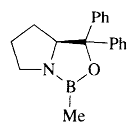
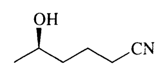
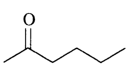
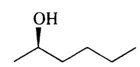
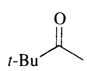
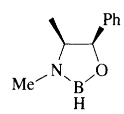
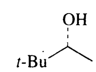
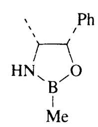
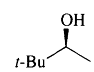
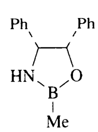
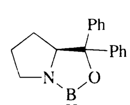
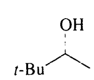
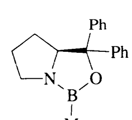
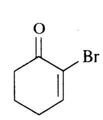
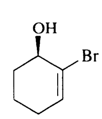
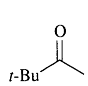
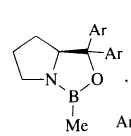
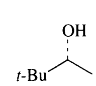
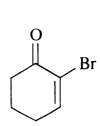
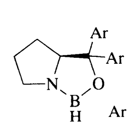
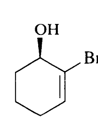
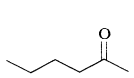
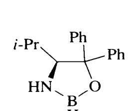
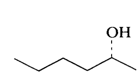
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		 (—) 66%	277a, 278
		 (—) 47%	277a, 278
		 (91) 94%	278
		 (83) 74%	278
	"	 (90) 66%	278
		 (96-100) 75%	76
		 (—) 82%	280
		" (—) 88%	280
	, 10 mol%	 (100) 92%	109
	, 10 mol%, −10°	" (100) 97%	110
	", 10 mol%, 23°	 (100) 91%	110
	, 10 mol%, 0° Ar = 2-naphthyl	 (>95) 93%	112
	, 10 mol%, 36° Ar = 2-naphthyl	 (>95) 91%	112
		 (100) 55%	100

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALOXAZABOROLIDINE CATALYSTS (*Continued*)

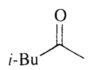
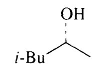
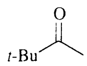
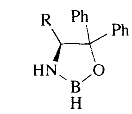
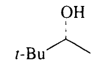
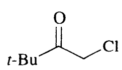
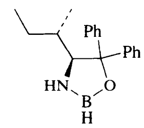
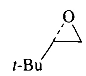
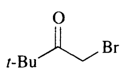
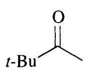
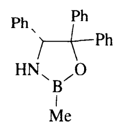
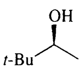
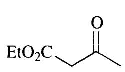
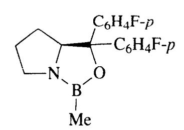
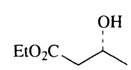
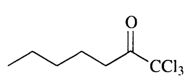
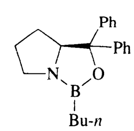
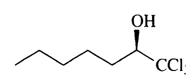
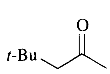
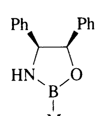
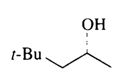
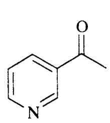
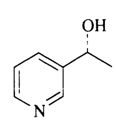
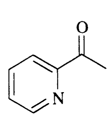
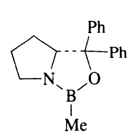
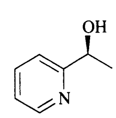
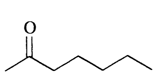
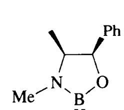
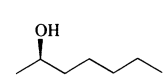
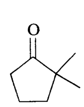
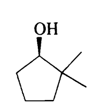
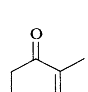
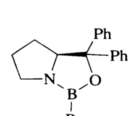
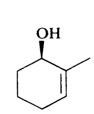
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
	"	 (100) 61%	100
		 R / Temp / (%) / ee Me / — / 100 / 72% *i*-Pr / — / " / 79% *i*-Bu / — / " / 55% *s*-Bu / 30° / " / 89% *s*-Bu / 0° / " / 96% Bn / — / " / 83% $MeS(CH_2)_2$ / — / " / 65%	100
		 (100) 90%	100
	"	" (100) 93%	100
	, 0°	 (90) 93%	281
		 (—) >99%	108
C_7			
	, catecholborane	 (96) 95%	127
	", catecholborane, −60°	" (—) 95%	282
		 (—) 76%	277a, 278
	"	 (—) 80%	277a, 278
		 (89) 45%	278
		 (96-100) 42%	76
	"	 (96-100) 76%	76
	, 10 mol%, catecholborane, −78°	 (>95) 93%	113

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

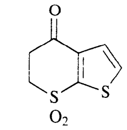
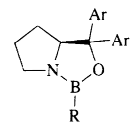
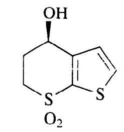
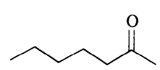
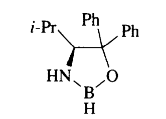
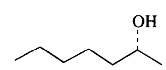
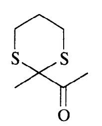
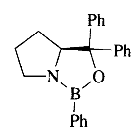
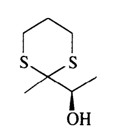
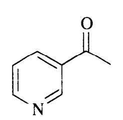
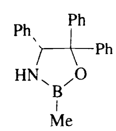
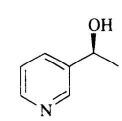
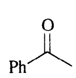
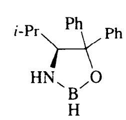
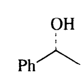
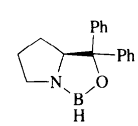
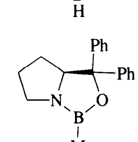
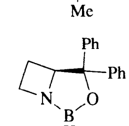
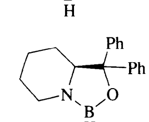
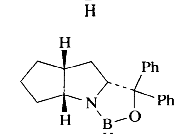
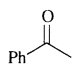
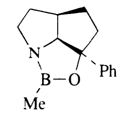
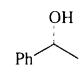
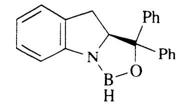
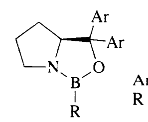
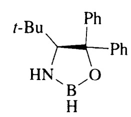
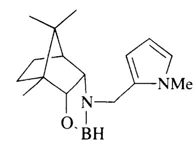
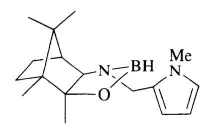
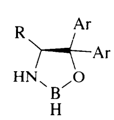
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee					Refs.
			Ar	R	(%)	ee	
			Ph	Me	—	96%	125
			C_6H_4F-*p*	Me	—	94%	
			C_6H_4Cl-*p*	Me	—	"	
			C_6H_4Me-*p*	Me	—	92%	
			$C_6H_4CF_3$-*p*	Me	—	96%	
			C_6H_4Bu-*t*--*p*	Me	—	90%	
			C_6H_4OMe-*p*	Me	—	94%	
			C_6H_4Cl-*m*	Me	—	92%	
			$C_6H_3Cl_2$-3,5	Me	—	"	
			$C_6H_3Me_2$-3,5	Me	—	"	
			2-naphthyl	Me	—	"	
			Ph	*n*-Bu	—	86%	
			Ph	Ph	—	96%	
			Ph	C_6H_4F-*p*	—	98%	
			Ph	C_6H_4Cl-*p*	—	96%	
			Ph	C_6H_4Me-*p*	—	98%	
			Ph	C_6H_4OMe-*p*	—	94%	
					(100)	56%	100
					(—)	94%	114
	 , 0°				(90)	95%	281
C_8							
					(100)	94%	100
		"			(100)	97%	109
		"			(100)	97%	110
		"			(100)	98%	283
		"			(100)	87%	284
		"			(100)	61%	285

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee			Refs.
			(100)	98%	286
		"	(100)	91%	287
	 Ar = 2-naphthyl R = H or Me	"	(100)	98%	112
		"	(100)	89%	287
		"	(100)	73%	288
		"	(100)	73%	288
		"			

R	Ar	(%)	ee	Refs.
$EtSCH_2$	Ph	80-95	83%	131
$MeS(CH_2)_2$	Ph	"	79%	130
$MeS(CH_2)_2$	*p*-MeC_6H_4	"	78%	130
i-$PrSCH_2$	Ph	95	70%	131

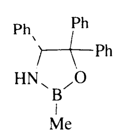
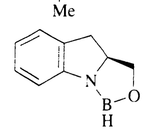
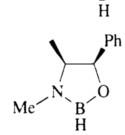
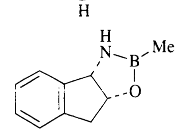
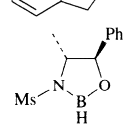
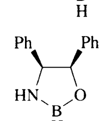
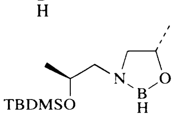
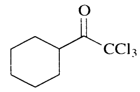
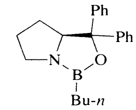
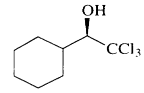
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee			Refs.
		"	(100)	96%	281
		"	(100)	97%	289
		"	(100)	72%	290
		"	(100)	86%	291
		"	(100)	72%	292
		"	(100)	>99%	293
		"	(100)	72%	294
	, catecholborane		(—)	92%	127

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

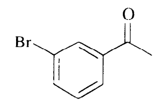
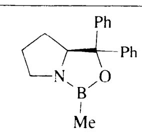
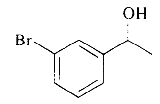
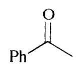
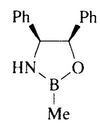
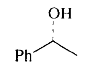
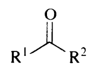
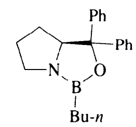
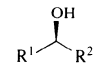
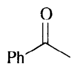
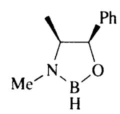
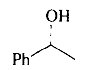
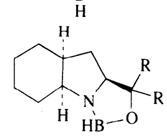
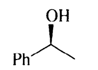
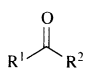
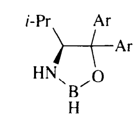
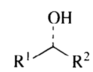
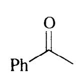
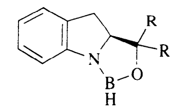
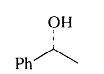
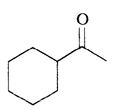
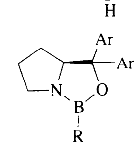
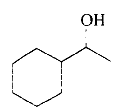
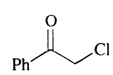
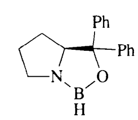
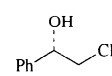
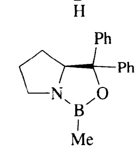
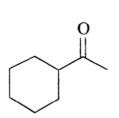
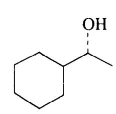
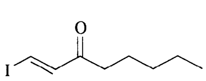
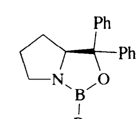
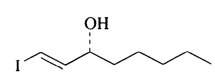
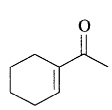
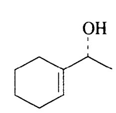
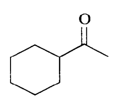
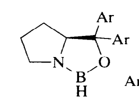
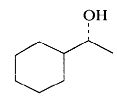
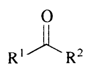
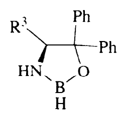
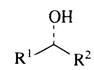
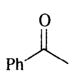
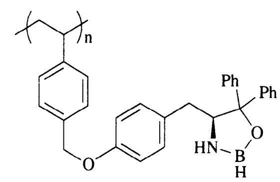
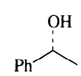
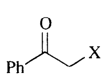
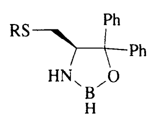
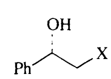
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		 (>90) 96%	294a
		 (—) 92%	277a, 278
	 , catecholborane	 R^1 | R^2 | Temp | (%) | ee *t*-Bu | CCl_3 | −20° | — | 98% *c*-C_6H_{11} | " | ND | — | 92% Ph | CF_3 | " | — | 90% " | CCl_3 | " | — | 96% " | CBr_3 | " | — | 98%	282
		 (96-100) 83%	76
		 R | (%) | ee H | 95 | 90% Ph | 96 | 49%	279
		 R^1 | R^2 | Ar | (%) | ee Ph | Me | *p*-$OMeC_6H_4$ | 76 | 93% Me | C_6H_{13} | " | 85 | 59% Ph | Me | *p*-FC_6H_4 | 100 | 93% Me | C_6H_{13} | " | 82 | 60% *c*-C_6H_{11} | Me | " | 85 | 72%	295
		 R | (%) | ee H | 96 | 82% Ph | 95 | 96%	279
		 R | Ar | (%) | ee Me | *p*-$CF_3C_6H_4$ | — | 76% *n*-Bu | Ph | — | "	125
	 , 5 mol %	 (100) 97%	109
	 , 10 mol%, 32°	" (100) 95%	110
	", 10 mol%, −10°	 (100) 84%	110
	 , 10 mol%, catecholborane, −78°	 (>95) 86%	113
	"	 (>95) 81%	113
	 , 10 mol%, 23° Ar = 2-naphthyl	 (>95) 85%	112

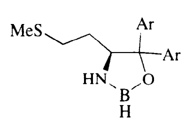
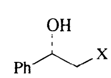
TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
			100

R^1	R^2	R^3	(%)	ee
n-C_6H_{13}	Me	i-Pr	100	58%
Ph	"	$(CH_2)_2SMe$	"	67%
"	"	Me	"	85%
"	"	i-Bu	"	82%
"	"	s-Bu	"	95%
"	"	Bn	"	87%
"	CH_2Cl	s-Bu	"	96%
"	CH_2Br	"	"	83%

Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		 (100) 76%	101
			131

X	R	(%)	ee
Cl	Et	80-95	97%
Br	"	"	100%
Cl	i-Pr	"	"
Br	"	"	"

Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
			130

X	Ar	(%)	ee
Cl	Ph	80-95	95%
Br	Ph	"	100%
Cl	p-MeC_6H_4	"	"
Br	"	"	"

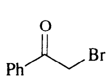
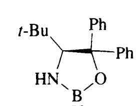
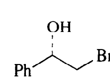
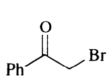
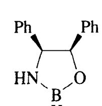
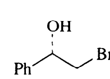
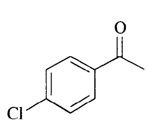
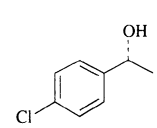
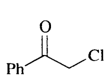
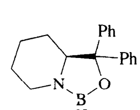
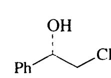
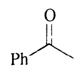
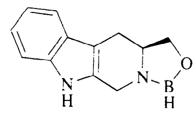
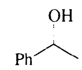
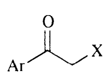
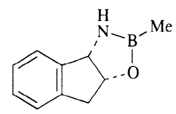
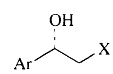
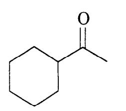
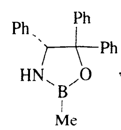
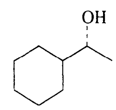
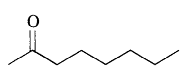
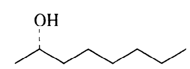
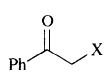
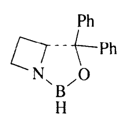
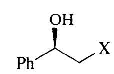
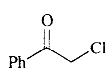
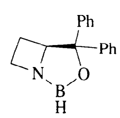
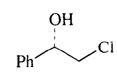
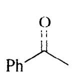
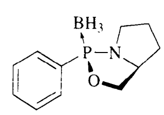
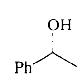
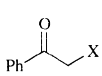
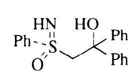
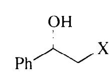
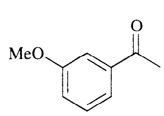
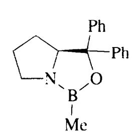
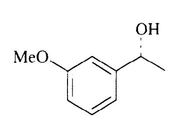
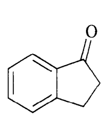
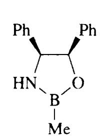
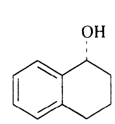
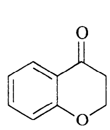
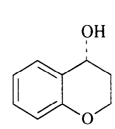
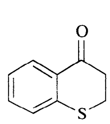
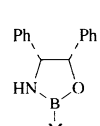
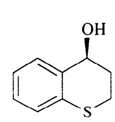
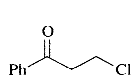
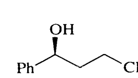
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		 (80-95) >95%	283
		 (100) >96%	293
	"	 (100) 89%	293
		 (85-95) 85%	284

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALOXAZABOROLIDINE CATALYSTS (*Continued*)

	Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
			 (85) 88%	296
				291
		, 0°	 (90) 82%	281
		"	 (90) 72%	281
		, 10 mol%		297
		, 10 mol%	 (90) 97%	297
		, toluene, 110°	 (—) >99%	108
C_9		, BH_3		140
			 (>90) 97%	294a
			 (—) 90%	277a, 278
		"	 (—) 97%	277a, 278
			 (—) 90%	277a, 278
		"	 (—) 84%	277a, 278

Ref. 291 (Ar–CO–CH_2X):

Ar	X	Temp	(%)	ee
Ph	Cl	–20°	>95	96%
p-BrC_6H_4	Br	"	"	97%
p-$NO_2C_6H_4$	Br	"	"	89%
Ph	H	0°	"	86%

Ref. 297 (Ph–CO–CH_2X):

X	(%)	ee
H	>90	95%
Cl	"	"

Ref. 140 (Ph–CO–CH_2X):

X	(%)	ee
H	75-85	76%
Cl	"	84%

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

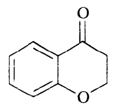
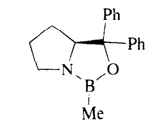
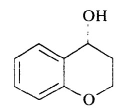
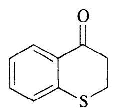
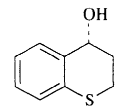
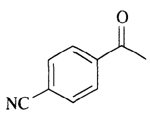
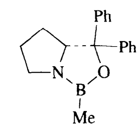
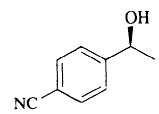
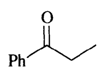
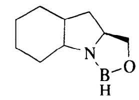
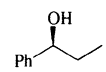
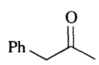
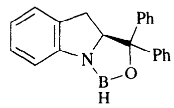
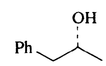
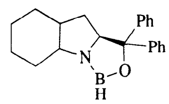
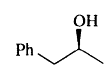
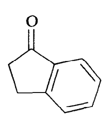
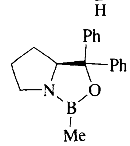
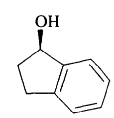
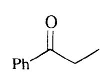
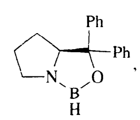
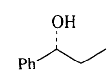
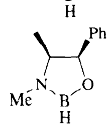
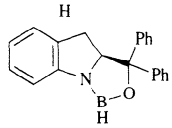
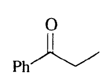
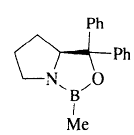
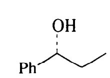
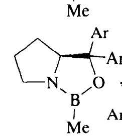
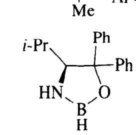
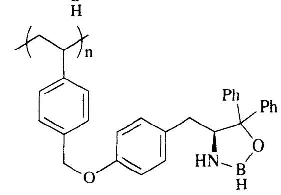
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee			Refs.
			(92)	96%	278
	"		(94)	92%	278
			(90)	94%	278
			(94)	85%	279
			(93)	92%	279
			(91)	86%	279
			(—)	96%	125
	, 5 mol%		(100)	90%	109
		"	(96-100)	79%	76
		"	(92)	90%	279
	, 10 mol%, –10°		(100)	97%	110
	, 10 mol%, 23° Ar = 2-naphthyl	"	(>95)	97%	112
		"	(100)	94%	100
		"	(100)	79%	101

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

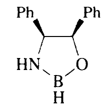
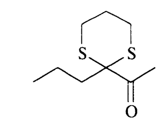
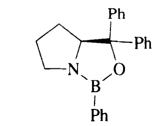
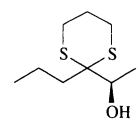
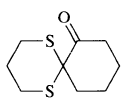
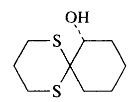
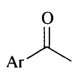
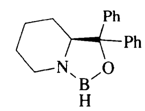
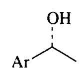
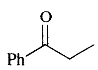
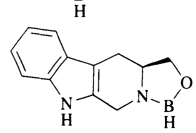
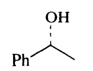
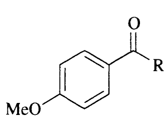
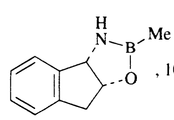
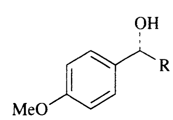
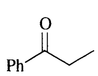
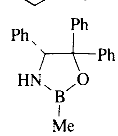
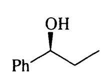
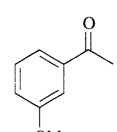
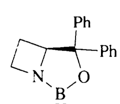
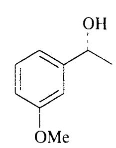
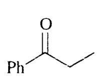
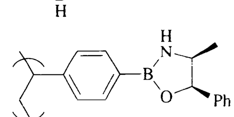
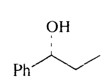
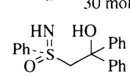
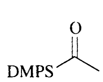
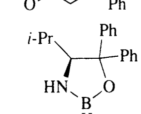
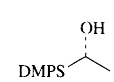
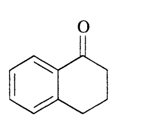
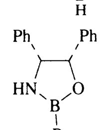
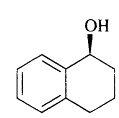
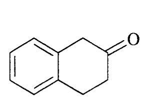
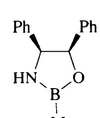
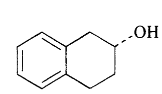
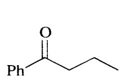
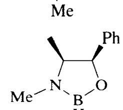
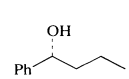
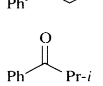
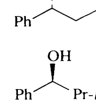
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		" (100) 79%	293
		 (—) 93%	114
	"	 (—) >96%	114
		 Ar / (%) / ee: *p*-$MeOC_6H_4$ / 85-95 / 90% *m*-$MeOC_6H_4$ / " / 92%	284
		 (97) 78%	296
	 , 10 mol%	 R / Temp / (%) / ee: CH_2Br / −20° / >95 / 97% Me / 0° / " / 90%	291
	 , 0°	 (90) 94%	281
	 , 10 mol%	 (>90) 95%	297
	 30 mol%, 20°	 (98) 89%	138
	 , BH_3	" (75-85) 73%	140
C_{10}			
		 (56) 50%	298
		 R / Config* / (%) / ee: H / (*S*, *R*) / — / 86% Me / " / — / 94% *n*-Bu / " / — / 90% Ph / " / — / 88% Me / (*R*, *S*) / — / 94% (*R*) *Configuration of modifier	277a, 278
		 (—) 30%	277a, 278
		 (96-100) 81%	76
	"	 (96-100) 56%	76

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

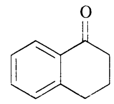
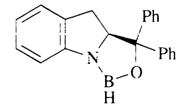
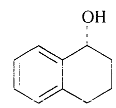
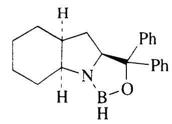
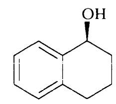
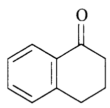
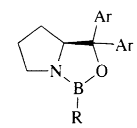
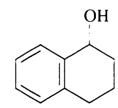
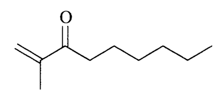
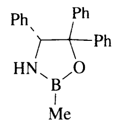
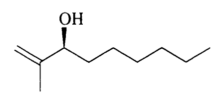
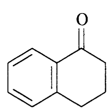
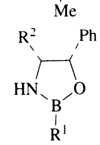
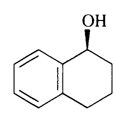
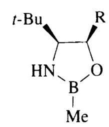
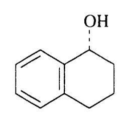
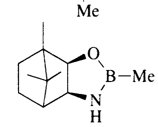
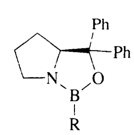
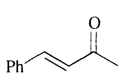
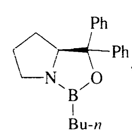
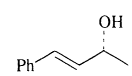
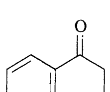
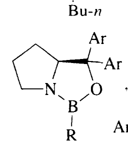
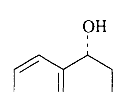
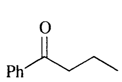
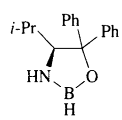
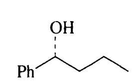
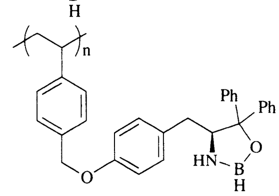
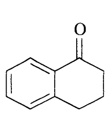
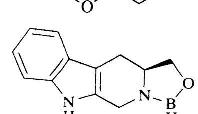
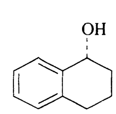
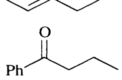
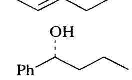
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
		 (91) 79%	279
		 (92) 79%	279
		 Ar / R / (%) / ee Ph / *n*-Bu / — / 96% *m*-ClC_6H_4 / Me / — / "	125
		 (—) 92% ee	299
		 R^1 / R^2 / (%) / ee Bu / Ph / — / 90% H / " / — / 86% Me / Me / — / 80%	280
		 R / (%) / ee H / — / 70% Ph / — / 82%	280
		" (—) 80%	280
		" R / (%) / ee H / 100 / 89% Me / " / 86%	109, 110
	 , 10 mol% catecholborane, −78°	 (>95) 92%	113
	 , 10 mol% Ar = 2-naphthyl	 R / Temp / (%) / ee H / 23° / >95 / 95% Me / 31° / " / "	112
		 (100) 96%	100
		" (100) 88%	101
		 (99) 96%	296
	"	 (96) 89%	296

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

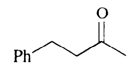
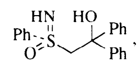
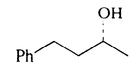
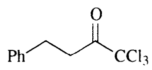
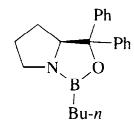
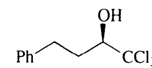
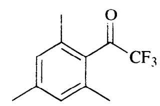
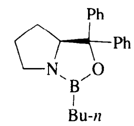
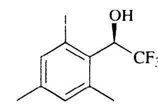
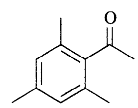
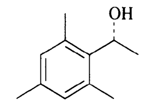
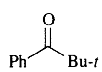
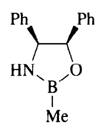
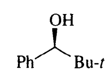
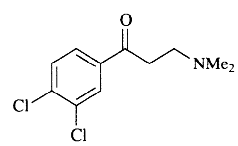
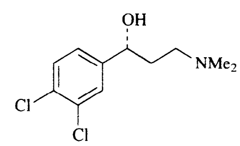
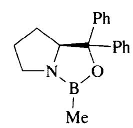
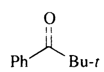
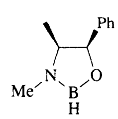
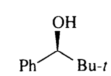
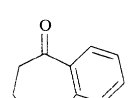
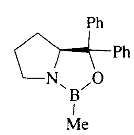
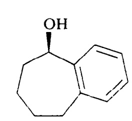
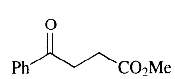
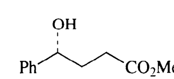
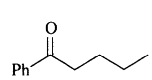
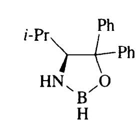
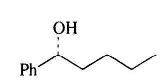
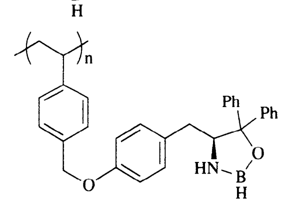
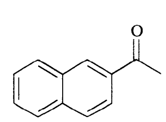
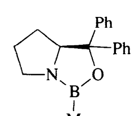
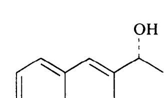
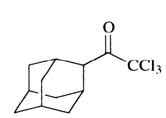
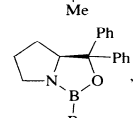
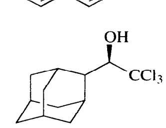
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
	, BH_3	 (75-85) 70%	140
	, catecholborane, −78°	 (—) 95%	282
C_{11} 	, catecholborane	 (100) 100%	300
	"	 (95) 99.7%	300
		 (—) 92%	277a, 278
	"	 (—) 94%	277a, 278
		" (92) 90%	278
		 (96-100) 74%	76
		 (—) 94%	125
	", 10 mol%, 0°	 (100) 94%	110
		 (100) 100%	100
		" (100) 97%	101
C_{12} 		 (>90) 96%	294a
	, catecholborane	 (—) 98%	282

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

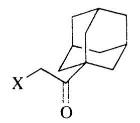
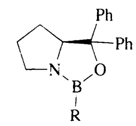
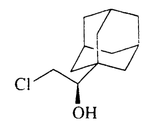
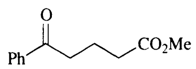
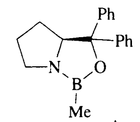
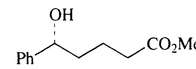
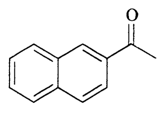
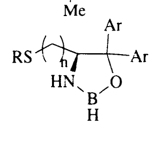
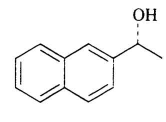
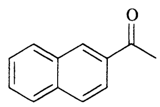
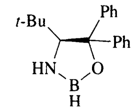
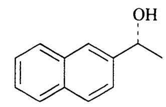
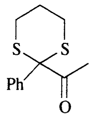
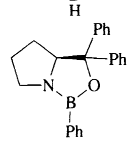
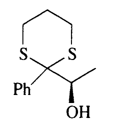
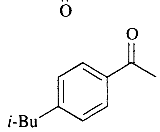
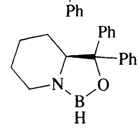
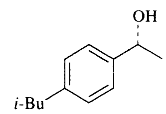
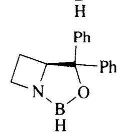
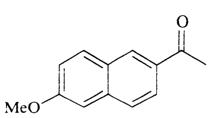
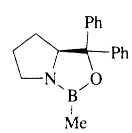
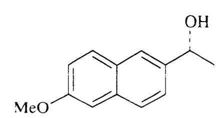
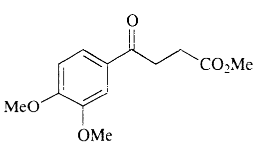
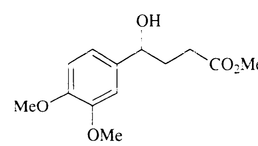
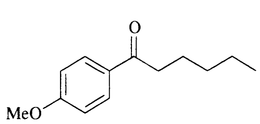
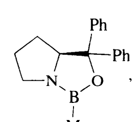
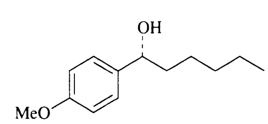
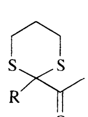
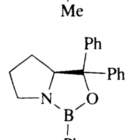
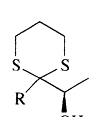
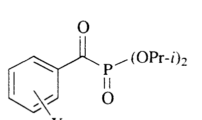
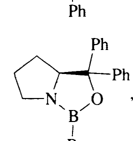
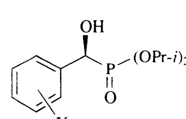
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee		Refs.
			X, R, (%), ee: Cl, *n*-Bu, >95, 71% Br, ", ", 89% ", Ph, ", 96%	301
	, 10 mol%, 0°		(100) 97%	110
			R, n, Ar, (%), ee: Et, 1, Ph, 80-95, 88% (131) *i*-Pr, 1, Ph, ", 83% (131) Me, 2, Ph, ", 77% (130) Me, 2, *p*-MeC_6H_4, ", 84% (130)	131, 131, 130, 130
			(80-95) 72%	283
			(—) 90%	114
			(85-95) 89%	284
	, 10 mol%	"	(>90) 95%	297
C_{13} 	, 10 mol%, 23°		(100) 98%	110
	", 2 mol%, 0°		(98) 95%	110
	, 10 mol%, −10°		(99) 96%	113
			R, (%), ee: Bn, —, 96% TBDMSOCH$_2$, —, 95%	114
	, catecholborane, −20°		X, (%), ee: H, 92, 65% 2-Cl, 96, 97% 3-Cl, 84, 77% 4-Cl, 98, 70% 2,4-diCl, 85, 94% 2-Br, 82, 95% 2-I, 79, 92% 2-F, 68, 91% 2,5-diF, 96, 99%	129

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRALOXAZABOROLIDINE CATALYSTS (*Continued*)

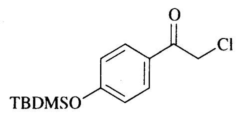
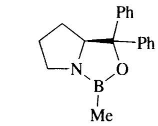
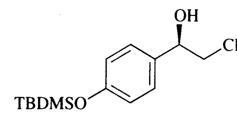
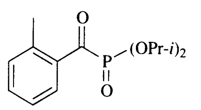
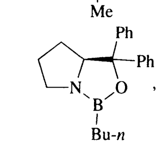
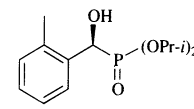
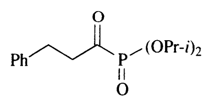
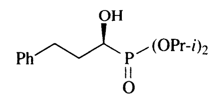
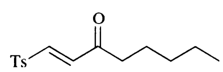
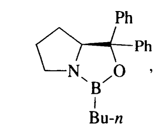
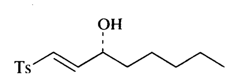
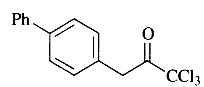
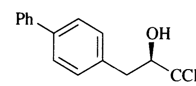
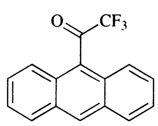
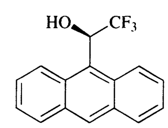
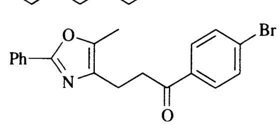
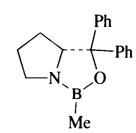
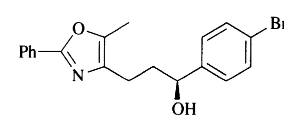
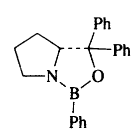
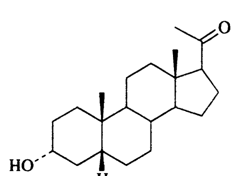
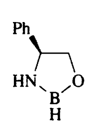
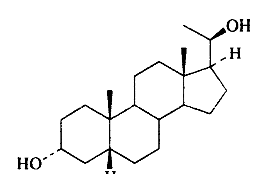
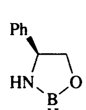
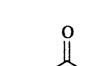
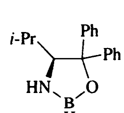
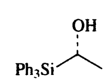
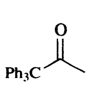
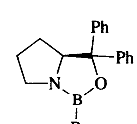
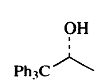
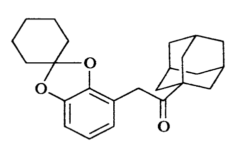
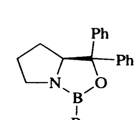
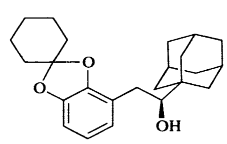
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
C_{14} 		 (96) 97%	302
	 , catecholborane, –20°	 (89) 97%	129
C_{15} 	"	 (85) 90%	129
	 , 10 mol% catecholborane, –78°	 (>95) 91%	113
	", 10 mol%, –44°	 (—) 96%	128
C_{16} 	", 10 mol%, catecholborane, –78°	 (>95) 94%	113
C_{19} 		 (>95) 94%	278
		" (>95) 90%	278
		 (100) 20*R* : 20*S* = 100 : 0	303
		" (69) 20*R* : 20*S* = 100 : 0	303
C_{20} 		 (71) 94%	298
C_{21} 	 , catecholborane	 (96) 97%	300
C_{24} 		 (46) 78%	301

TABLE III. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL OXAZABOROLIDINE CATALYSTS (*Continued*)

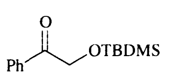
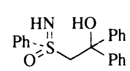
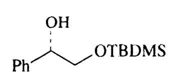
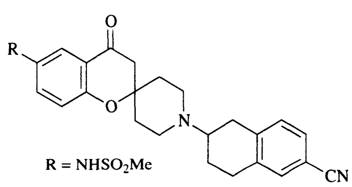
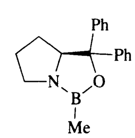
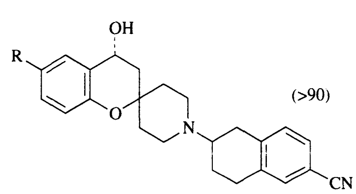
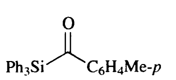
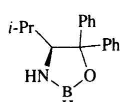
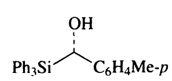
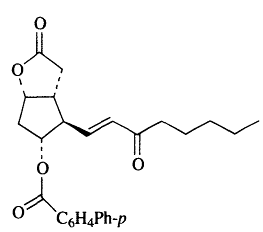
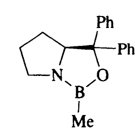
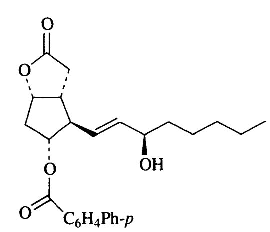
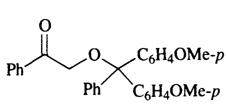
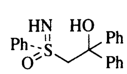
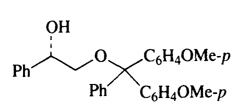
Ketone	Chiral Oxazaborolidine	Product(s), Yield(s) (%), and ee	Refs.
	 , BH_3	 (75-85) 92%	140
C_{25}  R = $NHSO_2Me$		 (>90) 98%	304
C_{26} 		 (87) 81%	298
C_{28} 	 , 10 mol%, 23°	 15*R* : 15*S* = 91 : 9	110
C_{29} 	 , BH_3	 (75-85) 93%	140

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS

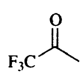
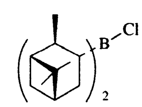
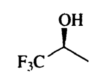
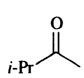
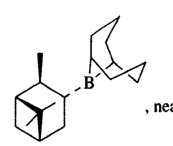
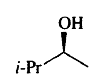
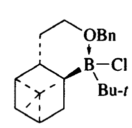
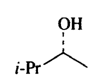
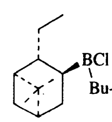
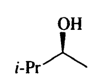
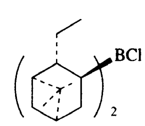
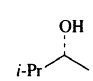
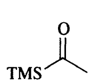
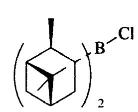
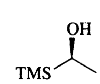
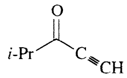
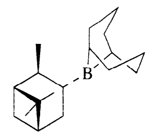
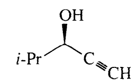
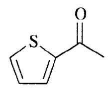
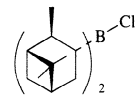
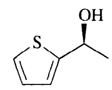
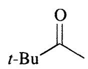
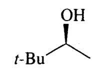
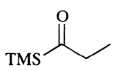
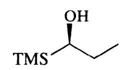
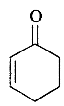
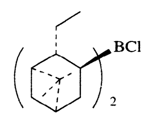
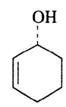
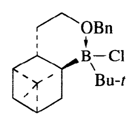
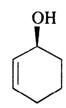
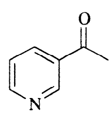
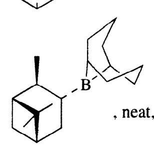
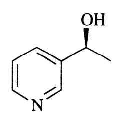
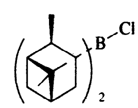
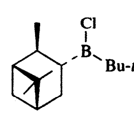
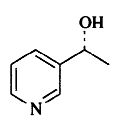
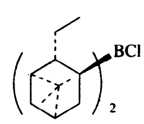
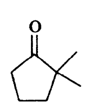
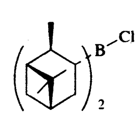
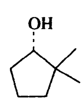
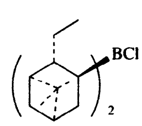
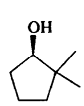
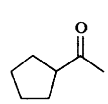
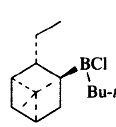
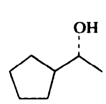
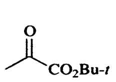
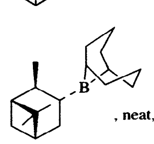
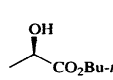
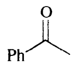
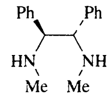
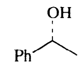
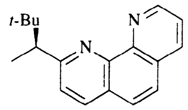
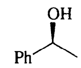
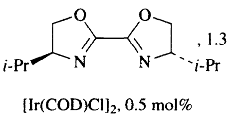
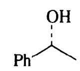
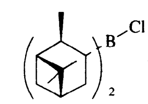
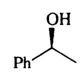
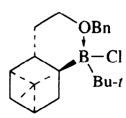
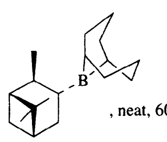
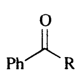
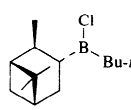
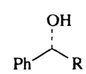
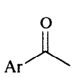
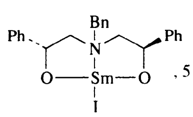
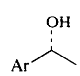
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
C_4			
		 (72) 96%	168
C_5			
	 , neat, 0°, 24 h	 (47) 90%	305
		 (100) 89%	166
		 (65) 84%	166
		 (65) 95%	170
		 (67) 96%	306

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

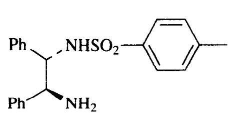
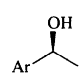
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
C_6					
			(78)	99%	158
	", neat, 25°, 4 days	"	(87)	99%	161
			(85)	91%	163
	"		(50)	95%	163, 307
	"		(62)	98%	306
			(60)	74%	170
			(79)	88%	166
C_7					
	 , neat, 6000 atm, 1.5 days		(67)	100%	305
		"	(67)	92%	163
			(62)	96%	165
		"	(60)	>99%	170
			(71)	98%	163
			(68)	>99%	170
			(65)	72%	166
	 , neat, 0°, 24 h		(98)	100%	161

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
C_8 	 , $[Rh(C_6H_{10})Cl]_2$, KOH, rt		(100)	67%	148
	 $[Rh(COD)Cl]_2$		(89)	63%	147
	 , 1.3 mol% $[Ir(COD)Cl]_2$, 0.5 mol% KOH, 2 mol%		(89)	58%	152
	 , 1 M, −25°		(72)	98%	163
		"	(50)	80%	166
	 , neat, 6000 atm, 24 h	"	(80)	100%	305
					165

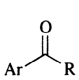
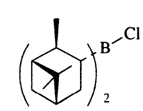
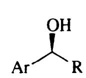
R	(%)	ee
H	68	96%
CH_2Cl	"	98%

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
	 , 5 mol %, THF		146

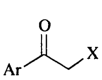
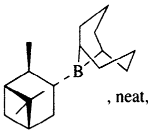
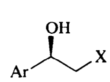
Ar	(%)	ee
Ph	74	96%
o-ClC_6H_4	96	97%
p-ClC_6H_4	88	94%
p-$O_2NC_6H_4$	77	94%

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
	 $[RuCl_2(mesitylene)]_2$, KOH		154

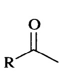
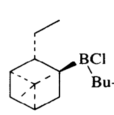
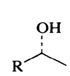
Ar	(%)	ee
Ph	95	97%
m-ClC_6H_4	98	98%
p-ClC_6H_4	95	93%

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
			164

Ar	R	(%)	ee
Ph	CH_2Cl	70-85	96%
2-BrC_6H_4	Me	"	99%
1,4-$Cl_2C_6H_3$	CH_2Cl	"	93%

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
	 , neat, 25°		161

Ar	X	Time	(%)	ee
Ph	H	7 d	68	85%
"	Cl	6-8 d	91	96%
"	Br	4 d	95	93%
"	I	2 d	60	"
p-BrC_6H_4	Br	3 d	95	96%

Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
			166

R	(%)	ee
Ph	70	81%
c-C_6H_{11}	83	90%

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

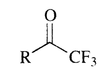
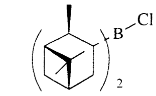
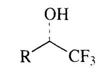
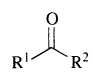
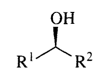
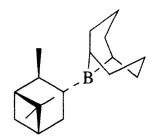
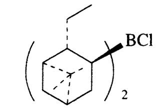
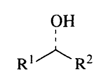
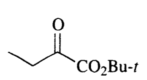
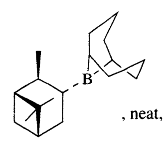
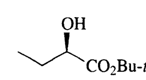
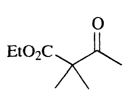
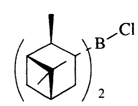
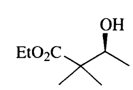
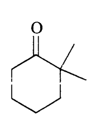
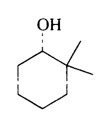
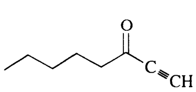
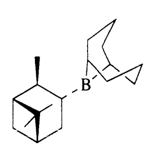
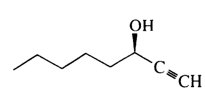
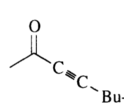
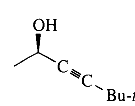
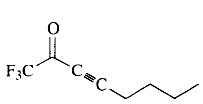
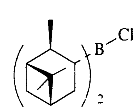
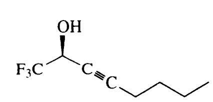
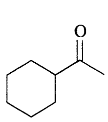
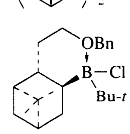
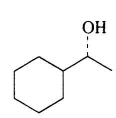
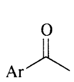
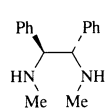
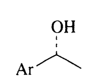
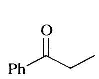
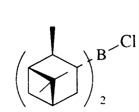
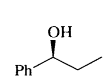
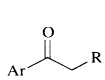
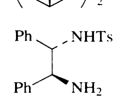
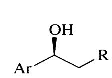
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
		 R (%) ee Ph 90 90% " 82 92% " 81 87% c-C_6H_{11} 75 "	168
	"	 R^1 R^2 (%) ee Ph CH_2F 80 95% " CHF_2 60 85% CF_3 n-C_6H_{13} 74 91%	169
		" R^1 R^2 (%) ee Ph CH_2F 71 89% " CHF_2 69 97% CF_3 n-C_6H_{13} 72 60%	169
		 R^1 R^2 (%) ee Ph Me 80 >99% " CH_2Cl 65 " c-C_6H_{11} Me " 97%	170
	, neat, 0°, 24 h	 (71) 100%	161
		 (69) 84%	163
	"	 (85) 91%	163
		 (65) 92%	158
	"	 (62) 73%	158
		 (76) >99%	167
		 (60) 96%	166
C_9			
	, $[Rh(C_6H_{10})Cl]_2$ KOH, rt	 Ar (%) ee p-NCC_6H_4 100 73% o-$CF_3C_6H_4$ " 68%	149
		 (62) 98%	163
	, $[RuCl_2(mesitylene)]_2$, KOH	 Ar R (%) ee Ph Me 94 97% o-Me H 53 91% m-OMe " 96 96%	154

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

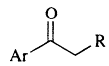
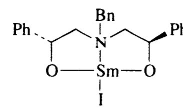
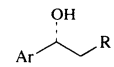
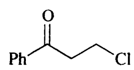
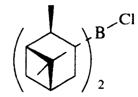
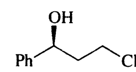
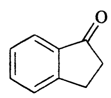
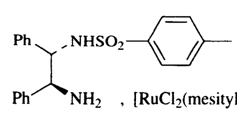
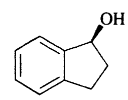
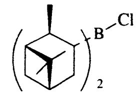
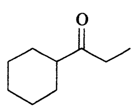
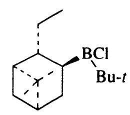
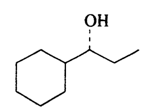
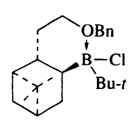
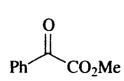
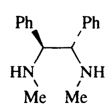
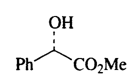
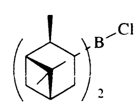
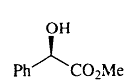
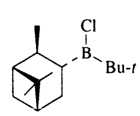
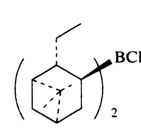
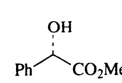
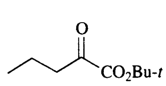
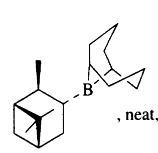
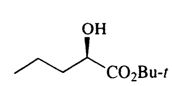
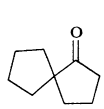
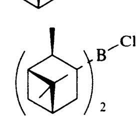
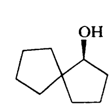
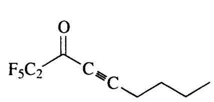
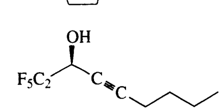
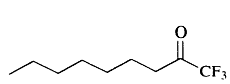
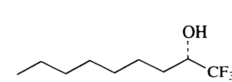
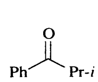
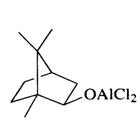
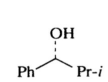
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee					Refs.
			Ar	R	(%)	ee	
	 , 5 mol%, THF		Ph	Me	63	73%	146
			o-OMe	H	95	96%	
			p-OMe	"	36	92%	
			o-Cl	Me	78	68%	
			(70-85) 97%				164
	 , $[RuCl_2(mesitylene)]_2$, KOH		(45) 91%				154
		"	(62) 97%				163
			(67) 73%				166
		"	(30) 85%				166
	 , $[Rh(C_6H_{10})Cl]_2$ KOH, rt		(100) >99%				148
			(—) 70%				163
		"	(70) 91%				164
			(78) 70%				170
	 , neat, 0°, 24 h		(79) 100%				161
			(65) 100%				163
	"		(72) 96%				167
	"		(80) 92%				168
C_{10}							
			(—) 70%				143

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

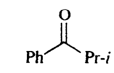
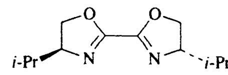
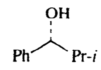
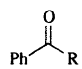
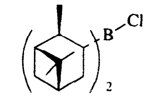
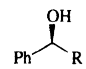
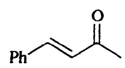
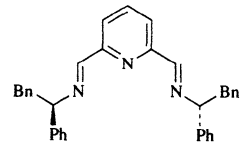
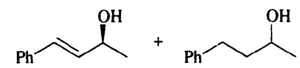
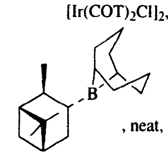
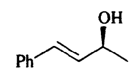
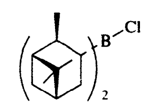
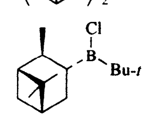
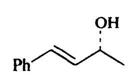
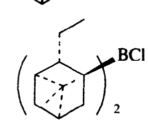
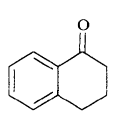
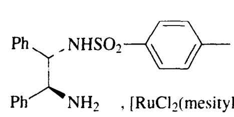
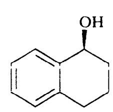
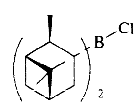
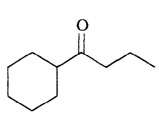
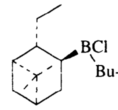
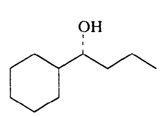
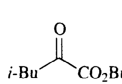
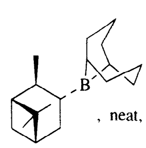
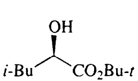
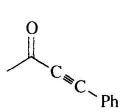
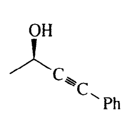
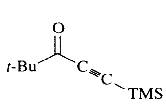
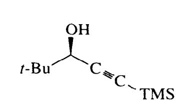
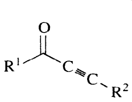
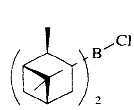
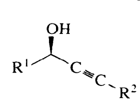
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
	 , 1.3 mol% $[Ir(COD)Cl]_2$, 0.5 mol%; KOH, 2 mol%	 (70) 91%	152
		 R / (%) / ee: *n*-Pr 77 100%; *i*-Pr 68 90%	163
	 $[Ir(COT)_2Cl]_2$, KOH	 94:6 (43) 82%	308
	 , neat, 25°, 10 d	 (80) 97%	161
		" (65) 81%	163
		 (72) 85%	164
		" (60) 82%	170
	 , $[RuCl_2(mesitylene)]_2$, KOH	 (65) 97%	154
		" (70) 86%	163
		 (67) 73%	170
	 , neat, 0°, 24 h	 (72) 100%	161
	", 0.5 M, THF, 25°	 (98) 78%	158
	", neat, 25°, 8-12 d	" (95) 100%	161
	", neat, 0°, 2.5 d	 (—) 100%	305
		 R^1 / R^2 / (%) / ee: CF_3 Ph 81 98%; C_3F_7 *n*-Bu 72 92%	169

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

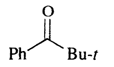
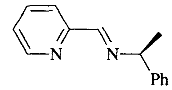
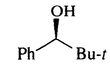
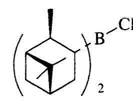
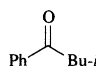
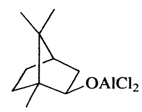
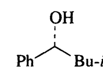
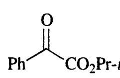
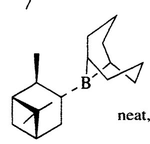
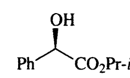
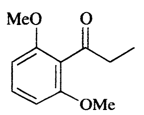
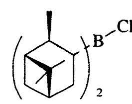
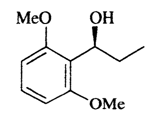
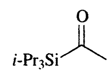
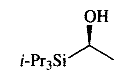
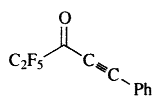
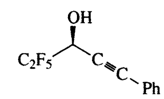
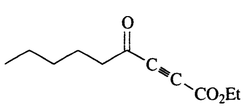
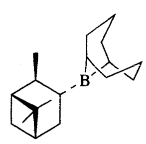
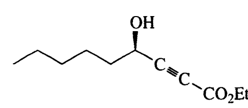
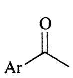
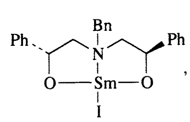
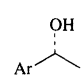
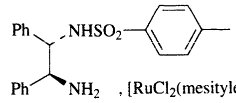
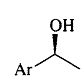
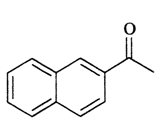
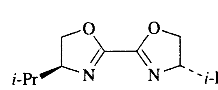
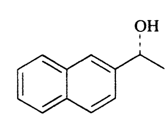
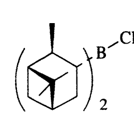
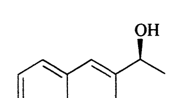
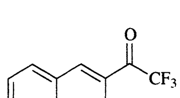
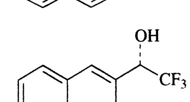
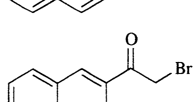
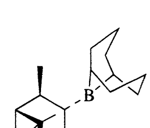
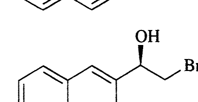
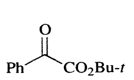
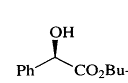
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee	Refs.
C_{11} 	 , $[IR(COD)Cl]_2$	 (91) 84%	150
		" (60) 79%	163
		 (—) 67%	143
	 neat, 25°, 2 d	 (91) 96%	161
		 (80) 96%	163
	"	 (64) 98%	306
	"	 (77) 96%	169
		 (72) 92%	158
C_{12} 	 , 5 mol%, THF	 Ar / (%) / ee 1-naphthyl 82 96% 2-naphthyl 95 97%	146
	 , $[RuCl_2(mesitylene)]_2$, KOH	 Ar / (%) / ee 1-naphthyl 93 98% 2-naphthyl 92 93%	154
	 , 1.3 mol%, $[Ir(COD)Cl]_2$, 0.5 mol% KOH, 2 mol%	 (94) 63%	152
		 (90) 98%	163
	"	 (92) 91%	168
		 (90) 90%	161
	", neat, 25°, 2 d	 (89) 100%	161

TABLE IV. ENANTIOSELECTIVE REDUCTION OF KETONES WITH MPV REAGENTS (*Continued*)

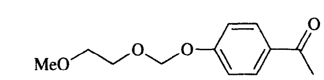
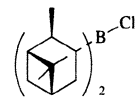
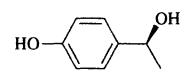
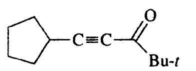
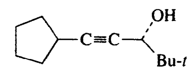
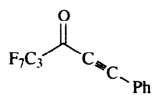
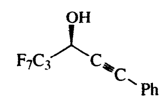
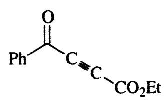
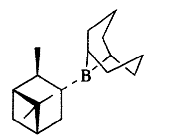
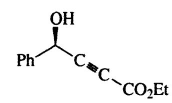
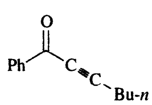
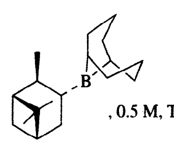
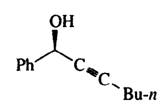
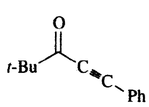
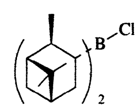
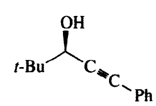
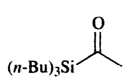
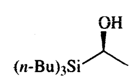
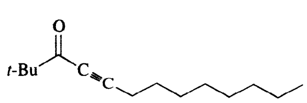
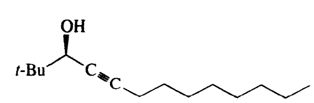
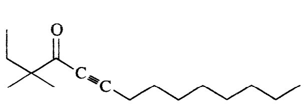
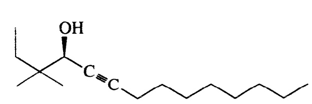
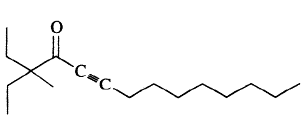
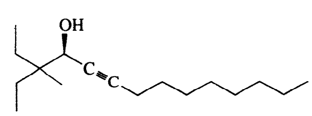
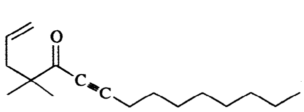
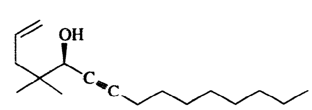
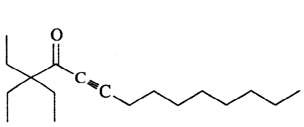
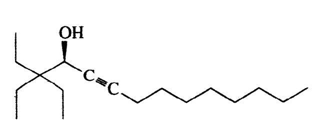
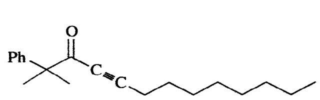
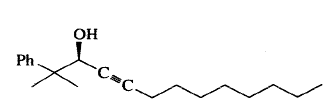
Ketone	Chiral Modifier	Product(s), Yield(s) (%), and ee			Refs.
			(65)	100%	305a
	"		(76)	97%	268
	"		(78)	94%	167
			(64)	100%	158
C_{13}					
	 , 0.5 M, THF, 25°		(72)	89%	158
			(80)	>99%	268
C_{14}					
	"		(59)	96%	306
C_{15}					
	"		(76)	>99%	268
C_{16}					
	"		(72)	>99%	268
C_{17}					
	"		(70)	>99%	268
	"		(71)	96%	268
C_{18}					
	"		(69)	>99%	268
C_{20}					
	"		(70)	97%	268

TABLE V. ENANTIOSELECTIVE HYDROGENATION OF KETONES USING TRANSITION METAL CATALYSTS

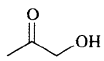
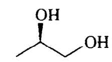
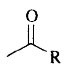
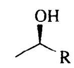
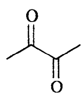
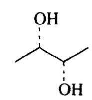
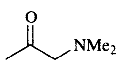
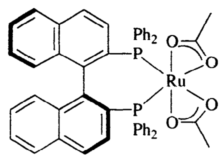
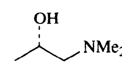
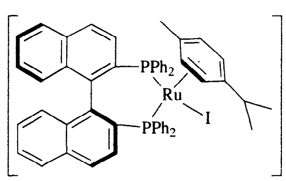
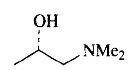
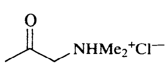
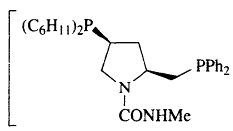
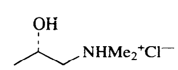
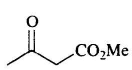
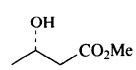
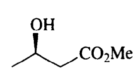
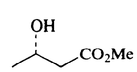
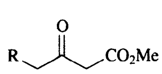
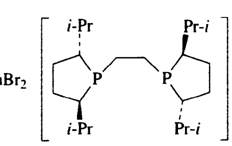
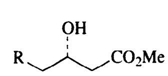
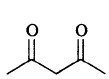
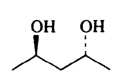
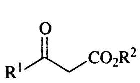
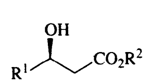
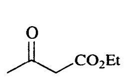
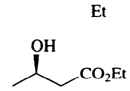
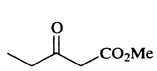
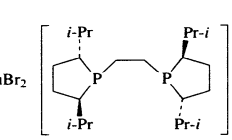
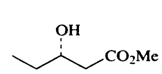
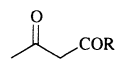
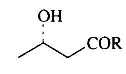
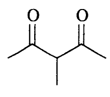
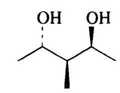
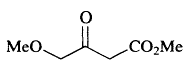
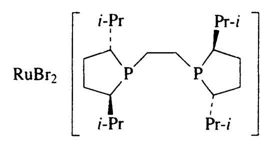
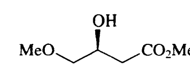
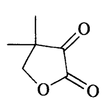
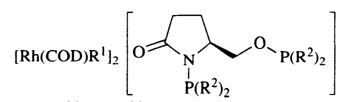
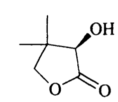
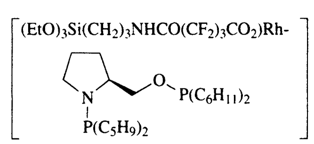
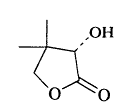
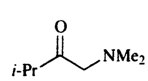
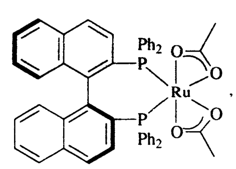
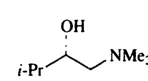
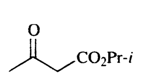
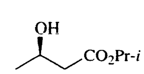
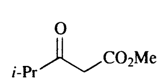
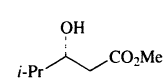
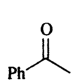
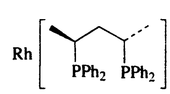
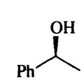
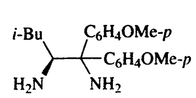
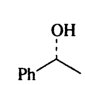
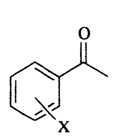
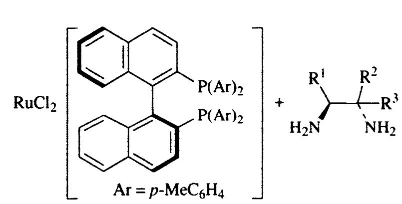
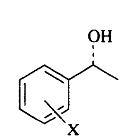
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
C_3			
	$RuCl_2$[(*R*)-BINAP], s/c = 230, 93 atm	 (100) 92%	181
C_4			
	$RuCl_2$[(*R*)-BINAP]	 R / s/c / Press / (%) / ee: CO_2Me / 780 / 96 atm / 97 / 83%; C_2H_4OH / 900 / 70 atm / 100 / 98%	181
	$RuBr_2$[(*S*)-BINAP], s/c = 680, 80 atm	 (100) 100% dl : meso = 26 : 74	181
C_5			
	 , s/c = 780, H_2, 50 atm	 (—) 96%	181
		 (—) 99%	182
	$[Rh(COD)Cl]_2$  0.01 mol%, 50°, H_2, 20 kg/cm^2	 (100) 86%	185
	$RuCl_2$[(*S*)-BINAP], s/c = 1400, 83 atm	 (97) >99%	189
	$RuCl_2$[(*R*)-BINAP], s/c = 2000, 100 atm	 (99) >99%	189
	$RuBr_2$[(*R*)-BINAP], s/c = 2100, 100 atm	" (99) >99%	189
	RuI_2[(*S*)-BINAP], s/c = 1400, 83 atm	 (99) >99%	189
	$RuBr_2$  , H_2, 60 psi MeOH/H_2O = 9/1	 R / (%) / ee: H / 100 / 99%; Cl / 100 / 76%	309
	$RuCl_2$[(*R*)-BINAP], s/c = 2000, 72 atm	 (100) 100%	181
C_6			
	RuX_2[(*R*)-BINAP]	 R^1 / R^2 / X / s/c / press / (%) / ee: Me / Et / Cl / 1000 / 103 atm / 99 / 99%; Et / Me / Br / 1200 / 98 atm / " / 100%	189
	$RuBr_2$[(*R*)-BINAP], s/c = 1260, 86 atm	 (100) 99%	181
	$RuBr_2$  , H_2, 60 psi MeOH/H_2O = 9/1	 (100) 99%	309

TABLE V. ENANTIOSELECTIVE HYDROGENATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	RuX$_2$[(*S*)-BINAP]	 R / X / s/c / press / (%) / ee NMe$_2$ / Br / 680 / 63 atm / 100 / 96% SEt / Cl / 540 / 95 atm / 42 / 93%	181
	RuCl$_2$[(*S*)-BINAP], s/c = 2200, 94 atm	 (100) 99%	181
	, H$_2$, 60 psi MeOH/H$_2$O = 9/1	 (100) 96%	309
	 s/c = 200, H$_2$, 50 atm	 R^1 / R^2 / (%) / ee Cl / C$_6$H$_{11}$ / — / 97% " / C$_5$H$_9$ / — / 96% O$_2$CCF$_3$ / C$_6$H$_{11}$ / — / 98% " / C$_5$H$_9$ / — / 99%	188
	, H$_2$, 1 atm	 (99-100) 91-94%	192
C$_7$			
	, s/c = 390, H$_2$, 100 atm	 (—) 95%	181
	RuBr$_2$[(*R*)-BINAP], s/c = 1100, 73 atm	 (93) 98%	189
	RuCl$_2$[(*R*)-BINAP], s/c = 1100, 100 atm	 (99) >99%	189
C$_8$			
	, Et$_3$N, H$_2$, 69 atm	 (—) 82%	194
	(*S*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 4 atm	 (>99) 87%	196
	 KOH, 2-propanol, s/c = 500		196

X	R^1	R^2	R^3	press	(%)	ee
o-Cl	Ph	Ph	H	50 atm	>99	94%
m-Cl	*i*-Pr	*p*-MeOC$_6$H$_4$	*p*-MeOC$_6$H$_4$	8	96	90%
p-Cl	"	"	"	"	>99	94%

TABLE V. ENANTIOSELECTIVE HYDROGENATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

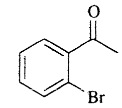
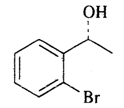
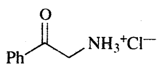
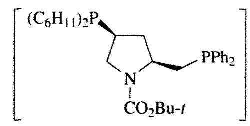
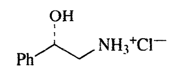
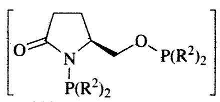
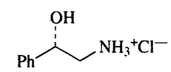
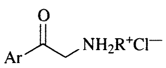
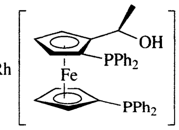
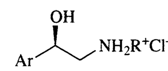
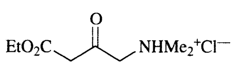
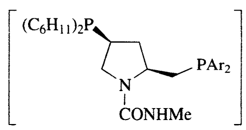
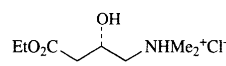
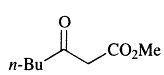
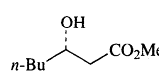
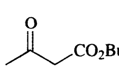
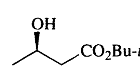
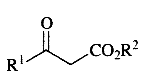
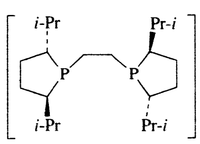
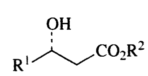
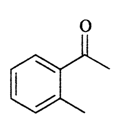
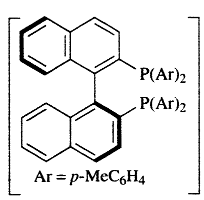
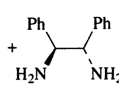
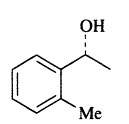
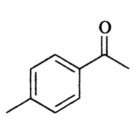
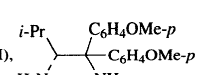
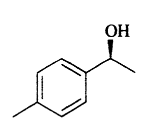
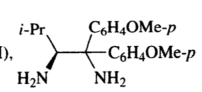
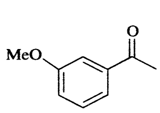
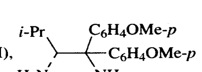
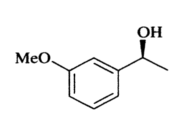
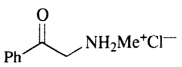
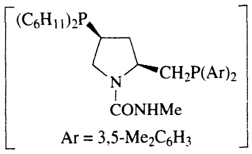
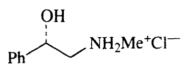
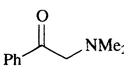
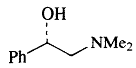
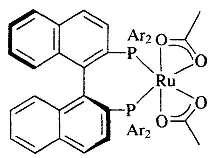
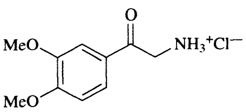
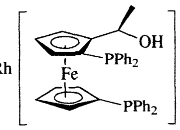
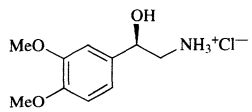
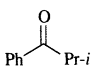
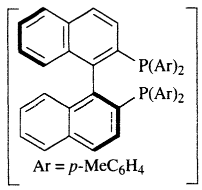
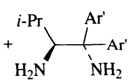
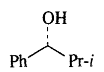
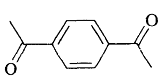
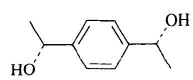
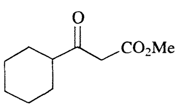
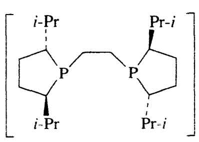
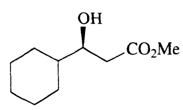
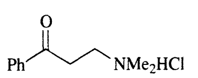
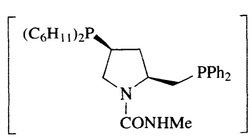
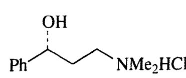
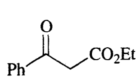
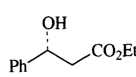
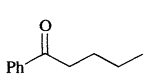
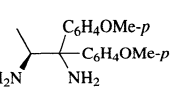
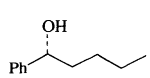
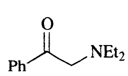
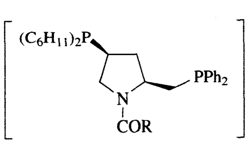
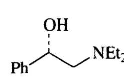
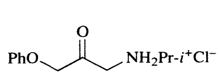
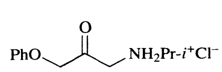
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	$RuBr_2$[(*R*)-BINAP], s/c = 1100, 100 atm	 (97) 92%	181
	$[Rh(COD)Cl]_2$  s/c = 1000, H_2, 20 atm	 (—) 81%	183
	$[Rh(COD)R^1]_2$  H_2, 50 atm, s/c = 200	 R^1 / R^2 / (%) / ee Cl / C_6H_{11} / — / 93% " / C_5H_9 / — / 83% $OCOCF_3$ / C_6H_{11} / — / 93% " / C_5H_9 / — / 83%	188
	Rh , s/c = 100, H_2, 50 atm	 Ar / R / (%) / ee Ph / H / 100 / 60% 4-HOC_6H_4 / " / " / 69% 3,4-HOC_6H_3 / Me / " / 95%	174
	$[Rh(COD)Cl]_2$  s/c = 100, H_2, 20 atm	 Ar / (%) / ee Ph / 100 / 83% 3,5-$Me_2C_6H_3$ / " / 85%	186
	$RuCl_2$[(*S*)-BINAP], s/c = 850, 94 atm	 (99) 98%	189
	$RuCl_2$[(*R*)-BINAP], s/c = 1000, 70 atm	 (98) 98%	189
	$RuBr_2$ , H_2, 60 psi, MeOH/H_2O = 9/1	 R^1 / R^2 / (%) / ee Me / *t*-Bu / 100 / 99% *n*-Pr / Et / " / " *i*-Pr / " / " / "	309
C_9			
	$RuCl_2$  Ar = *p*-MeC_6H_4 +  KOH, 2-propanol, s/c = 500, 4 atm	 (>99) 94%	196
	(*R*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 4 atm	 (>99) 91%	196
	(*R*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 4 atm	" (>99) 92%	196
	(*R*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 8 atm	 (>99) 88%	196

TABLE V. ENANTIOSELECTIVE HYDROGENATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

Ketone	Conditions	Product(s), Yield(s) (%), and ee			Refs.
	[Rh(COD)Cl]$_2$  s/c = 1000, H_2, 20 atm		(—)	81%	183
C_{10}					
	[$RuBr_2$(BINAP)], s/c = 490, H_2, 100 atm		(—)	95%	181
	 , s/c = 530, H_2, 100 atm Ar = *p*-MeC_6H_4	"	(—)	93%	181
	Rh  , s/c = 100, H_2, 50 atm		(100)	90%	174
	$RuCl_2$  +  Ar' = *p*-$MeOC_6H_4$ KOH, 2-propanol, s/c = 500, 8 atm		(>99)	95%	196
	"		(98)	>99%	196
	$RuBr_2$  , H_2, 60 psi, MeOH/H_2O = 9/1		(100)	99%	309
C_{11}					
	[Rh(COD)Cl]$_2$  0.01 mol%, H_2, 20 kg/cm^2, 50°		(100)	64%	185
	$RuBr_2$[(*R*)-BINAP], s/c = 760, 91 atm		(100)	85%	189
	(*S*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 4 atm		(>99)	90%	196
C_{12}					
	[Rh(COD)Cl]$_2$  H_2, 20 atm		R / s/c / (%) / ee OBu-*t* / 10^3 / — / 93% NHMe / " / — / 97% " / 10^5 / — / 96%		183
	" , 0.01 mol%, 20 kg/cm^2, 50°		(100)	87%	185

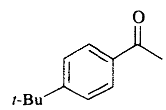
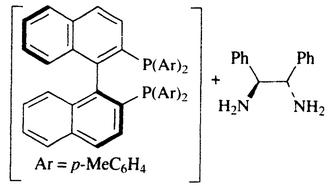
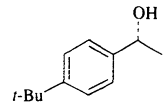
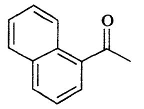
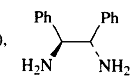
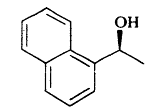
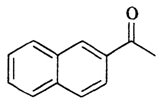
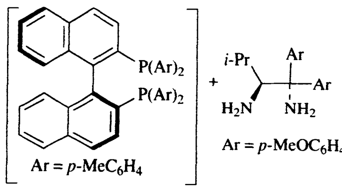
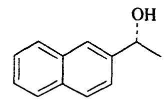
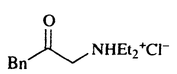
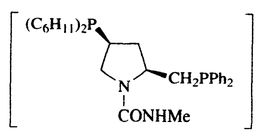
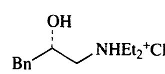
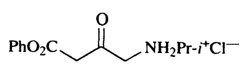
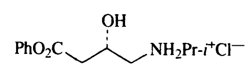
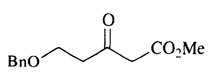
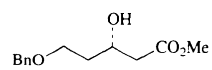
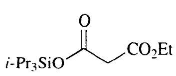
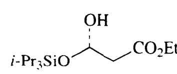
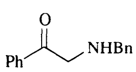
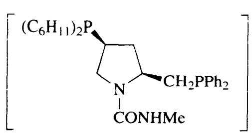
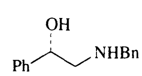
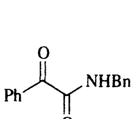
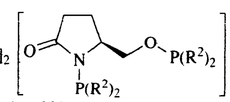
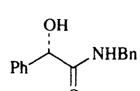
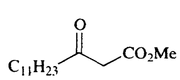
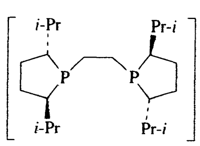
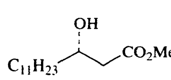
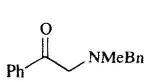
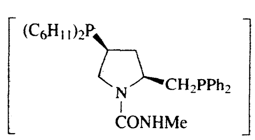
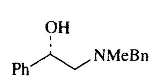
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	$RuCl_2$  Ar = *p*-MeC_6H_4 KOH, 2-propanol, s/c = 500, 50 atm	 (>99) 96%	196
	(*S*)-BINAP-Ru(II),  KOH, 2-propanol, s/c = 500, 4 atm	 (>99) 97%	196
	$RuCl_2$  Ar = *p*-MeC_6H_4; Ar = *p*-$MeOC_6H_4$ KOH, 2-propanol, s/c = 500	 Temp / press / (%) / ee ND / 1 atm / 99 / 95% –22° / 50 atm / 98 / 97%	196
C_{13}			
	$[Rh(COD)Cl_2]$  0.01 mol %, H_2, 20 kg/cm^2, 50°	 (100) 91%	185
	", s/c = 100, H_2, 20 atm	 (100) 87%	185
	$RuBr_2$[(*S*)-BINAP], s/c = 370, 50 atm	 (94) 99%	181
C_{14}			
	$RuBr_2$[(*S*)-BINAP], s/c = 290, 100 atm	 (100) 95%	181
C_{15}			
	$[Rh(COD)Cl]_2$  s/c = 1000, H_2, 20 atm	 (—) 93%	183
	$[Rh(COD)R^1]_2$  H_2, 50 atm, s/c = 200	 R^1 / R^2 / (%) / ee Cl / C_6H_{11} / — / 87% " / C_5H_9 / — / 80% $OCOCF_3$ / C_6H_{11} / — / 61% " / C_5H_9 / — / 67%	188
	$RuBr_2$ , H_2, 60 psi, MeOH/H_2O = 9/1	 (100) 99%	309
C_{16}			
	$[Rh(COD)Cl]_2$  s/c = 1000, H_2, 20 atm	 (—) 90%	183

TABLE V. ENANTIOSELECTIVE HYDROGENATION OF KETONES USING TRANSITION METAL CATALYSTS *(Continued)*

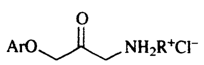
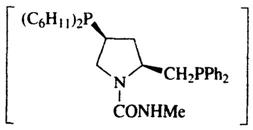
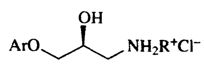
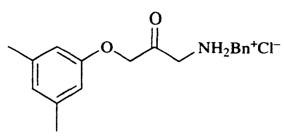
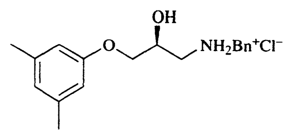
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
 Ar = 1-naphthyl	$[Rh(COD)Cl]_2$  0.01 mol %, H_2, 20 kg/cm^2, 50°	 Ar / R / (%) / ee: 1-naphthyl, *i*-Pr, 100, 91%; Ph, Bn, ", 97%	185
C_{18}			
	"	 (100) 95%	185

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS

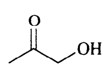
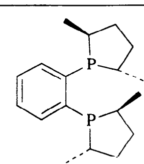
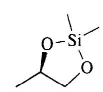
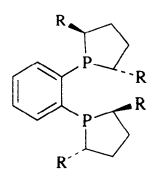
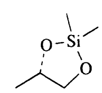
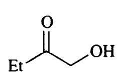
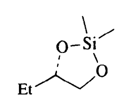
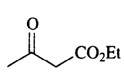
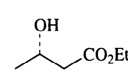
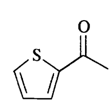
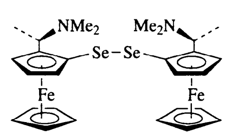
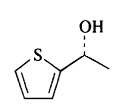
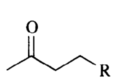
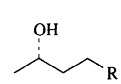
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
C_3			
	, Me_2SiHCl	 (—) 61%	218
	, Me_2SiHCl	 R (%) ee Et — 78% *i*-Pr — 93%	218
C_4			
	"	 (—) 92%	218
C_6			
	**130**, 4 mol%; **131**, 1 mol%; $AgBF_4$, 1 mol% Ph_2SiH_2, –5°, 24 h	 (60) 27%	210
	, $[Rh(COD)Cl]_2$, Ph_2SiH_2, rt	 (100) 78%	215
C_7			
	**130**, 6 mol%; **131**, 1 mol%; $AgBF_4$, Ph_2SiH_2	 R mol %* Temp Time (%) ee CO_2Et 2 0° 7 h 91 95% CH_2OAc 1 20° 24 h 85 68% *$AgBF_4$	210

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

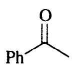
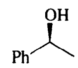
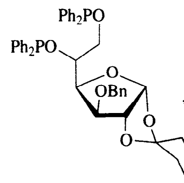
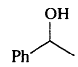
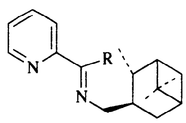
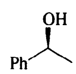
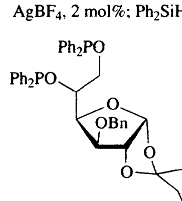
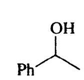
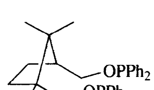
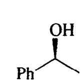
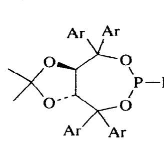
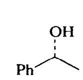
Ketone	Conditions	Product(s), Yield(s) (%), and ee			Refs.
C_8 	(*R, R*)-(−)-DIOP, $[Rh(COD)Cl]_2$, 1-$NpPhSiH_2$		(100)	58%	200
	 , $[Rh(C_2H_4)_2Cl]_2$, 1-$NpPhSiH_2$		(65)	65%	198
	 , $[Rh(COD)Cl_2]_2$, Ph_2SiH_2		(99)	79%	201, 310
	134b:Rh = 10:1; $[Rh(COD)Cl]_2$, CCl_4	"	(59)	84%	214
	130; **131**, 1 mol%; ethyl levulinate $AgBF_4$, 2 mol%; Ph_2SiH_2, 0°	"	**130** / Time / (%) / ee 4 mol% / 3 h / 94 / 95% none / 6 h / 86 / 83% 4 mol% / 2 h / 91 / 94%		210
	130, 4 mol%; **131**, 1 mol% $AgPF_6$, 2 mol%; Ph_2SiH_2, −3°, 5 h	"	(80)	87%	210
	130, 7 mol%; **131**, 1 mol% AgOTf, 1 mol%; Ph_2SiH_2, −5°, 27 h	"	(96)	89%	210
	130, 3.5 mol%; **131**, 1 mol% BF_3OEt_2, 1.5 mol%; Ph_2SiH_2, 0°, 14 h	"	(90)	82%	210
	130, 3.5 mol%; **131**, 1 mol% $EtAlCl_2$, 1.5 mol%; Ph_2SiH_2, 0°, 18 h	"	(89)	67%	210
	(*s*-Bu-PYBOX), 6 mol%, (*s*-Bu-PYBOX-$RuCl_3$), 1 mol% $AgBF_4$, 2 mol%; Ph_2SiH_2, −5°, 10 h	"	(91)	91%	210
	(*t*-Bu-PYBOX), 4 mol%, (*t*-Bu-PYBOX-$RuCl_3$), 1 mol% AgOTf, 2 mol%; Ph_2SiH_2, 0°, 18 h	"	(92)	83%	210
	132c, 4 mol%; **132c**-Rh, 1 mol% $AgBF_4$, 2 mol%; Ph_2SiH_2, −5°, 3 h	"	(90)	94%	211
	132b, 4 mol%; **132b**-Rh, 1 mol% $AgBF_4$, 2 mol%; Ph_2SiH_2, 10°, 18 h	"	(86)	93%	211
	132a, 4 mol%; **132a**-Rh, 1 mol% $AgBF_4$, 2 mol%; Ph_2SiH_2, 20°, 16 h	"	(83)	90%	211
	133, 4 mol%; **133**-Rh, 1 mol% $AgBF_4$, 2 mol%; Ph_2SiH_2, 5°, 2 h	"	(98)	90%	212
	 , 1-$NpPhSiH_2$		(65)	65%	198
	 , 1-$NpPhSiH_2$		(64)	51%	198
	 , $[Rh(COD)Cl]_2$ Ar = 1-naphthyl		(91)	82%	217

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

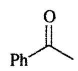
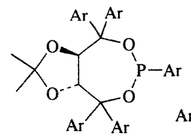
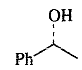
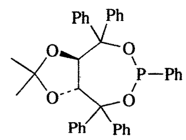
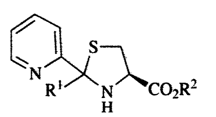
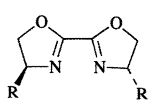
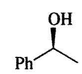
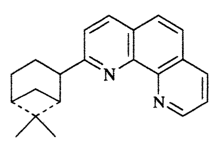
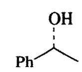
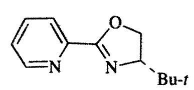
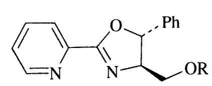
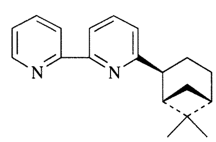
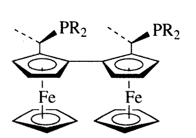
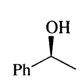
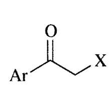
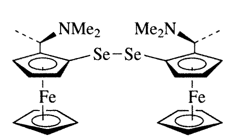
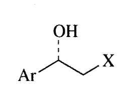
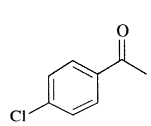
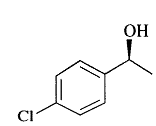
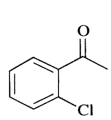
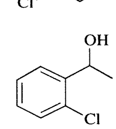
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	 , $[Rh(COD)Cl]_2$ Ar = 1-naphthyl	 (99) 84%	217
	 , $[Rh(COD)Cl]_2$	" (59) 55%	217
	 , $[Rh(COD)Cl]_2$, Ph_2SiH_2 Rh:ligand = 1:8	" R^1 / R^2 / (%) / ee H / Et / 90 / 88% Me / Me / " / 80%	205
	 , $[Rh(COD)Cl]_2$, 0.5 mol%	 R / mol % / Solv. / (%) / ee *i*-Pr / 6 / CCl_4 / — / 55% Bn / 5 / CCl_4 / 59 / 84% Bn / 5 / toluene / 72 / 50%	214
	 , 2.5 mol% $[Rh(COD)Cl]_2$, 0.5 mol% Ph_2SiH_2	 (—) 76%	311
	 , 2.5 mol% $[Rh(COD)Cl]_2$, 0.5 mol% Ph_2SiH_2	" Solvent / (%) / ee CCl_4 / 77 / 70% toluene / 90 / 83%	208
	 , $[Rh(C_2H_4)_2Cl]_2$, 1-NpPhSiH$_2$	" R / (%) / ee CPh_3 / 100 / 80% 2,5-$Me_2C_6H_3$ / 92 / 74%	209
	 , 2.5 mol% $[Rh(COD)Cl]_2$, 0.5 mol% Ph_2SiH_2	" (86) 72%	312
	 $[Rh(COD)_2]BF_4$, Ph_2SiH_2, –40°	 R / (%) / ee *n*-Bu / 88 / 92% *n*-Pr / 89 / "	216
	 $[Rh(COD)Cl]_2$, Ph_2SiH_2, rt	 Ar / X / (%) / ee Ph / H / 31 / 85% Ph / Cl / 85 / 88% *p*-$O_2NC_6H_4$ / H / 45 / 76%	215
	"	 (41) 74%	215
	**130**, 4 mol%; **131**, 1 mol% $AgBF_4$, 1 mol%; Ph_2SiH_2, 0°, 4 h	 (74) 94%	210

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

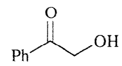
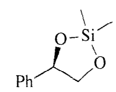
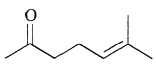
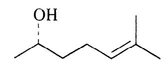
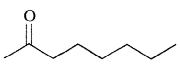
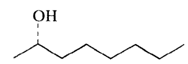
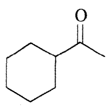
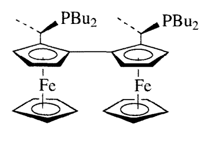
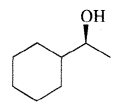
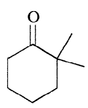
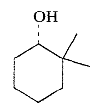
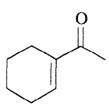
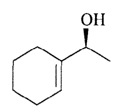
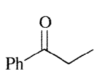
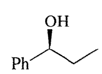
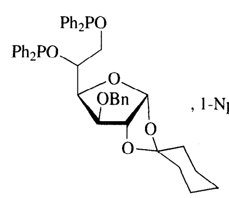
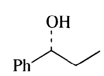
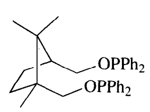
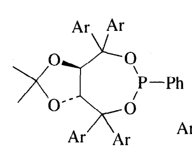
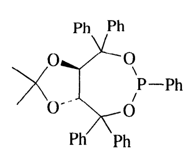
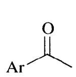
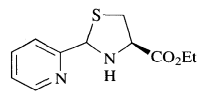
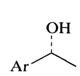
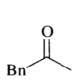
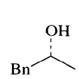
Ketone	Conditions	Product(s)	Yield(s) (%)	ee	Refs.
	Me_2SiHCl, (*S*, *S*)-**139a**		(—)	73%	218
	Me_2SiHCl, (*R*, *R*)-**139c**	"	(—)	67%	218
	**130**, 6 mol%; **131**, 1 mol% $AgBF_4$, 1 mol%; Ph_2SiH_2, 20°, 20 h		(94)	70%	210
	**130**, 4 mol%; **131**, 1 mol% $AgBF_4$, 1 mol%; Ph_2SiH_2, 0°, 2 h		(85)	63%	210
	 $[Rh(COD)_2]BF_4$, Ph_2SiH_2, –40°		(62)	80%	216
	"		(70)	88%	216
	"		(71)	95%	216
C_9					
	**130**, 4 mol%; **131**, 1 mol% $AgBF_4$, 1 mol%: Ph_2SiH_2, 5°, 4 h		(73)	91%	210
	 , 1-NpPhSiH$_2$		(65)	61%	198
	 , 1-NpPhSiH$_2$	"	(65)	52%	198
	 , $[Rh(COD)Cl]_2$ Ar = 1-naphthyl	"	(98)	66%	217
	 , $[Rh(COD)Cl]_2$	"	(59)	56%	217
	 $[Rh(COD)Cl]_2$, Ph_2SiH_2, Rh:ligand = 1:8		Ar (%) ee *p*-MeC_6H_4 95 86% *o*-MeC_6H_4 90 84%		205
	**130**, 6 mol%; **131**, 1 mol% $AgBF_4$, 1 mol%, $PhSiH_2$, 0°, 5 h		(95)	71%	210

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

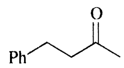
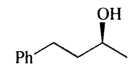
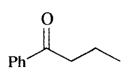
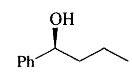
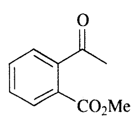
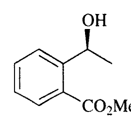
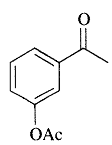
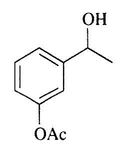
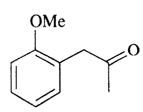
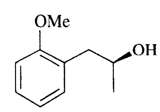
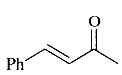
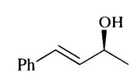
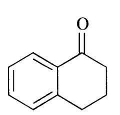
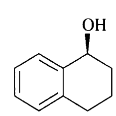
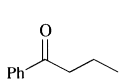
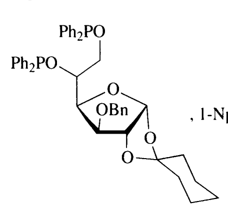
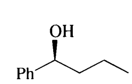
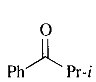
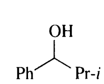
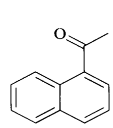
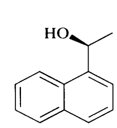
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
C_{10}			
	**132b**, 4 mol%, **132b**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 25°, 6 h	 (88) 51%	211
	132a, 4 mol%, **132a**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 30°, 17 h	" (96) 49%	211
	130, 4 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, –5°, 24 h	" (92) 66%	210
	132c, 4 mol%, **132c**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, –5°, 3 h	" (84) 80%	211
	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, 0-5°, 5 h	 (82) 82%	210
	**130**, 6 mol%, **131**, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 0°, 14 h	 (95) 96%	210
	**130**, 6 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, 0°, 24 h	 (81) 92%	210
	**130**, 6 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, –5°, 4 h	 (95) 82%	210
	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 0°, 7 h	 (91) 22%	210
	**132c**, 4 mol%, **132c**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, –5°, 2 h	 (93) 99%	211
	132b, 4 mol%, **132b**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 10°, 18 h	" (93) 99%	211
	132a, 4 mol%, **132a**-Rh, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 20°, 7 h	" (95) 97%	211
	130, 4 mol%, **131**, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, 0°, 2 h	" (92) 99%	210
	 , 1-NpPhSiH$_2$	 (60) 51%	198
	"	 (55) 34%	198
C_{12}			
	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 2 mol%, Ph_2SiH_2, –5°, 5 h	 (87) 94%	210

TABLE VI. ENANTIOSELECTIVE HYDROSILYLATION OF KETONES USING TRANSITION METAL CATALYSTS (*Continued*)

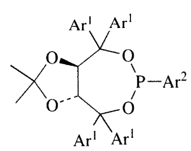
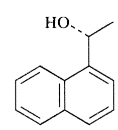
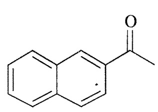
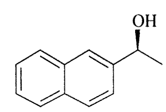
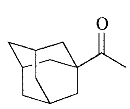
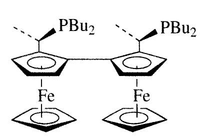
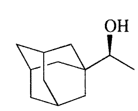
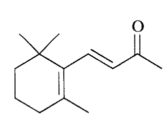
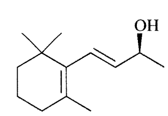
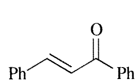
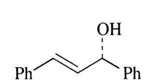
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	 , $[Rh(COD)Cl]_2$	 Ar[1] / Ar[2] / (%) / ee 1-naphthyl / Ph / 84 / 84% 1-naphthyl / 1-naphthyl / 92 / 87% Ph / Ph / 82 / 61%	217
	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, –5°, 6 h	 (93) 93%	210
	 $[Rh(COD)_2]BF_4$, Ph_2SiH_2, –40°	 (92) 91%	216
C_{13} 	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, 10°, 5 h	 (91) 44%	210
C_{15} 	**130**, 4 mol%, **131**, 1 mol% $AgBF_4$, 1 mol%, Ph_2SiH_2, 0°, 45 h	 (87) 71%	210

TABLE VII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH BAKER'S YEAST AND RELATED MICROORGANISMS

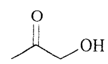
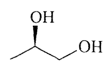
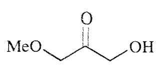
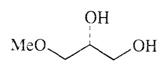
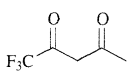
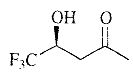
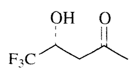
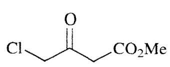
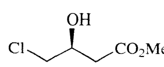
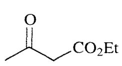
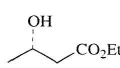
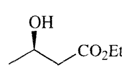
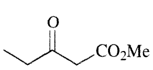
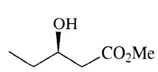
Ketone	Conditions	Product(s), Yield(s) (%), and ee			Refs.
C_3					
	Sucrose, phosphate buffer, 30°, 48 h		(—)	90%	244
C_4					
	"		(—)	88%	244
C_5					
	Allyl alcohol, glucose, 27-30°, 20-24 h		(82)	92%	254
	Allyl bromide, glucose, 27-30°, 20-24 h		(37)	81%	254
	Baker's yeast entrapped in polyurethane		(60-80)	90%	229
C_6					
	Free baker's yeast, 30°, 1 d		(60-80)	>98%	229
	Baker's yeast entrapped in calcium alginate, 30°, 1 d	"	(60-80)	92%	229
	Baker's yeast entrapped in polyurethane, 30°, 1 d		(60-80)	60%	229
	Baker's yeast entrapped in polyurethane		(60-80)	86%	229

TABLE VII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH BAKER'S YEAST AND RELATED MICROORGANISMS (*Continued*)

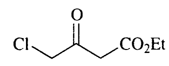
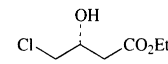
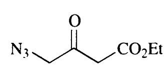
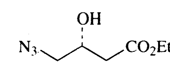
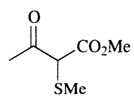
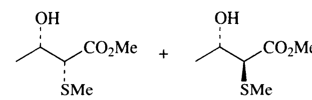
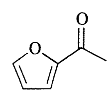
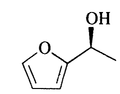
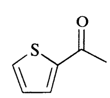
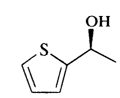
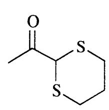
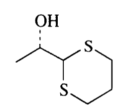
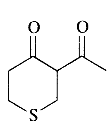
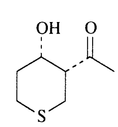
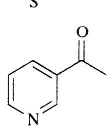
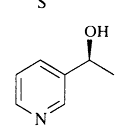
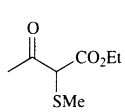
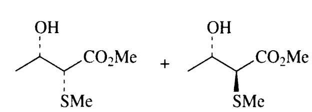
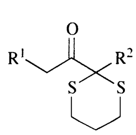
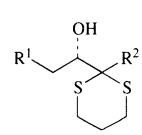
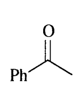
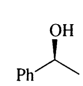
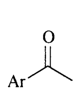
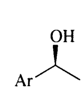
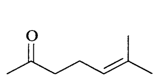
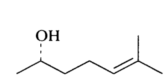
Ketone	Conditions	Product(s), Yield(s) (%), and ee			Refs.
	Free baker's yeast		(60-80)	42%	229
	Baker's yeast entrapped in polyurethane	"	(60-80)	82%	229
	Baker's yeast, D-glucose, pH 7.5-8, 25-30°		(70-80)	80%	230
	D-glucose, 2 d	 72 + 28	(72)	>96%, >96%	236
	Phosphate buffer pH 5, 5 d		(7)	80%	222
	Immobilized *Geotrichum candidum* 2-hexanol, hexane, 30°, 24 h	"	(81)	99%	223
	Sodium succinate, 3 d		(10)	86%	222
	Baker's yeast, D-glucose, $MgSO_4$		(84)	>96%	240
	Baker's yeast		(40)	95%	313
	Baker's yeast, glucose, 6 d		(100)	76%	222
	Baker's yeast, D-glucose, 2 d	 59 + 41	(62)	>96%, >96%	236
	Baker's yeast, D-glucose, $MgSO_4$		R^1 R^2 (%) ee Me H 71 >96% H Me 50 "		240
C_8					
	Baker's yeast, glucose, 4 d		(90)	100%	222
	Immobilized *Geotrichum candidum* 2-hexanol, hexane, 30°, 24 h		Ar (%) ee Ph 73 99% o-ClC_6H_4 99 " m-ClC_6H_4 88 " p-ClC_6H_4 41 92%		223
	Baker's yeast		(64)	92%	224

TABLE VII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH BAKER'S YEAST AND RELATED MICROORGANISMS *(Continued)*

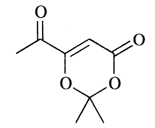
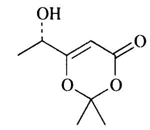
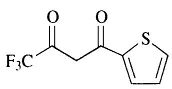
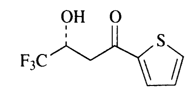
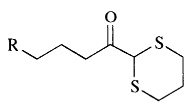
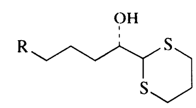
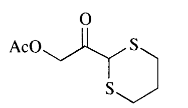
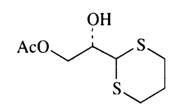
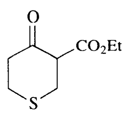
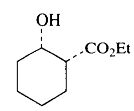
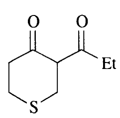
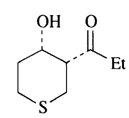
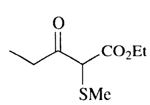
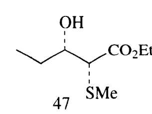
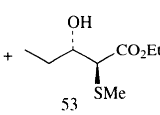
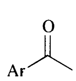
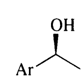
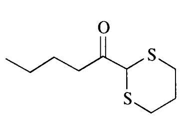
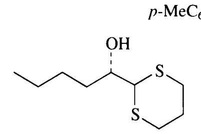
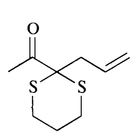
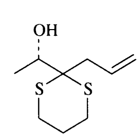
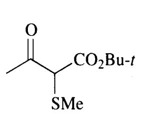
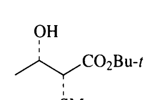
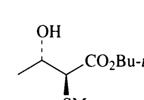
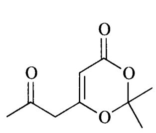
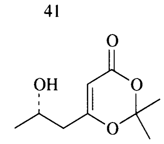
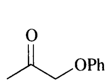
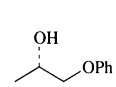
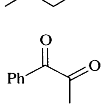
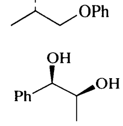
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	Baker's yeast, sucrose, 32°, 12 h	 (90) 91%	241
	Baker's yeast, allyl bromide, glucose 27-30°, 20-24 h	 (34) 81%	254
	Baker's yeast, D-glucose, $MgSO_4$	 R / (%) / ee: H 92 96%; OH 74 "	240
	Baker's yeast	 (58) 87%	245
	Baker's yeast	 (—) 85%	314
	Baker's yeast	 (66) 97%	313
	Baker's yeast, D-glucose, 2 d	 47 +  53 (44) >96%, >96%	236
C_9			
	Immobilized *Geotrichum candidum* 2-hexanol, hexane, 30°, 24 h	 Ar / (%) / ee: *o*-MeC_6H_4 59 99%; *m*-MeC_6H_4 60 "; *p*-MeC_6H_4 49 "	223
	Baker's yeast, D-glucose, $MgSO_4$	 (71) >96%	240
	"	 (31) >96%	240
	Baker's yeast, D-glucose, 2 d	 41 +  59 (75) >96%, >96%	236
	Sucrose, 32°, 12 h	 (44) 90%	241
	Sucrose, phosphate buffer 30°, 48 h	 (—) 91%	244
	Baker's yeast immobilized on chrysotile	 (23) 94%	315
	Baker's yeast immobilized on montmorillonite K 10	" (47) 93%	315

TABLE VII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH BAKER'S YEAST AND RELATED MICROORGANISMS (*Continued*)

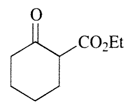
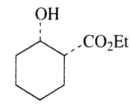
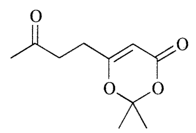
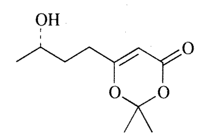
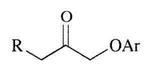
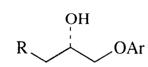
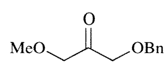
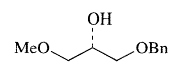
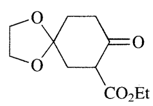
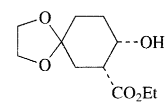
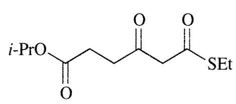
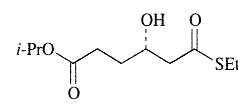
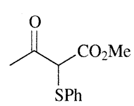
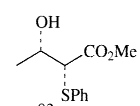
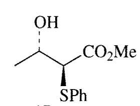
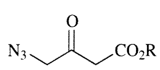
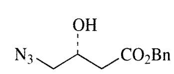
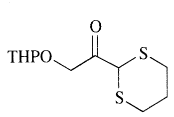
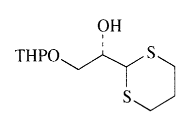
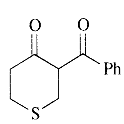
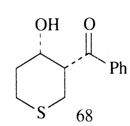
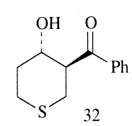
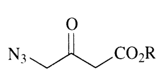
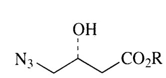
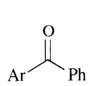
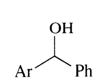
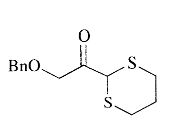
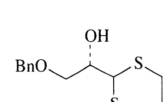
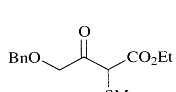
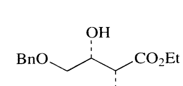
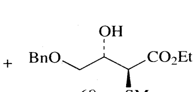
Ketone	Conditions	Product(s), Yield(s) (%), and ee	Refs.
	Baker's yeast	 (69) 86%	232
C_{10}			
	Baker's yeast, sucrose, 32°, 12 h	 (58) >99%	241
	Baker's yeast, sucrose phosphate buffer 30°, 48 h	 R / Ar / (%) / ee H / Bn / — / 90% OMe / Ph / 35 / 55%	244
C_{11}			
	"	 (—) 33%	244
	Baker's yeast	 (74) 98%	233
	Baker's yeast, 30°, 24 h	 (26) 84%	316
	Baker's yeast, D-glucose, 2 d	 83 +  17 (40) >96%, >96%	236
	Baker's yeast, D-glucose, pH 7.5-8, 25-30°	 R / (%) / ee Bn / 70-80 / 95% n-C_7H_{15} / " / 100%	230
	Baker's yeast	 (37) >95%	245
C_{12}			
	Baker's yeast	 68 +  32 (77) >99%, >99%	313
	Baker's yeast, D-glucose, pH 7.5-8, 25-30°	 R / (%) / ee C_2H_4Ph / 70-80 / 95% n-C_8H_{17} / " / 100%	230
	Free baker's yeast in water	 Ar / (%) / ee 4-pyridyl / 78 / 86% 3-pyridyl / 77 / 56%	255
	Immobilized baker's yeast in water	" Ar / (%) / ee 4-pyridyl / 86 / 84% 3-pyridyl / 65 / 45%	255
	Immobilized baker's yeast in hexane	" Ar / (%) / ee 4-pyridyl / 20 / 96% 3-pyridyl / 11 / 36%	255
C_{13}			
	Baker's yeast	 (50) >95%	245
C_{14}			
	Baker's yeast, D-glucose, 2 d	 32 +  68 (30) >96%, >96%	236

TABLE VIII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL DIHYDROPYRIDINE REAGENTS

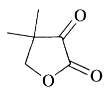
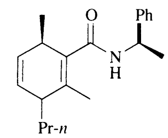
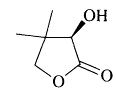
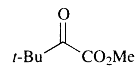
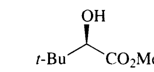
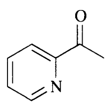
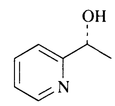
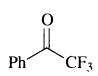
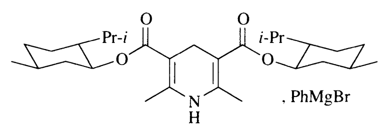
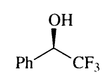
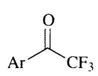
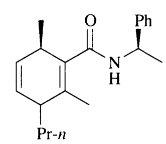
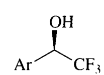
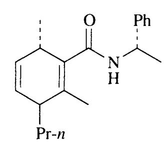
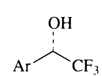
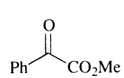
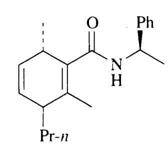
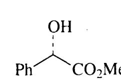
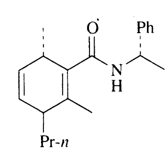
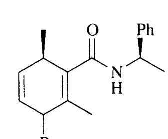
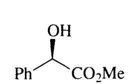
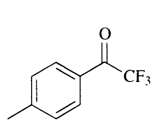
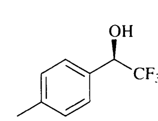
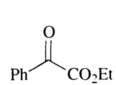
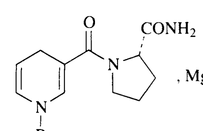
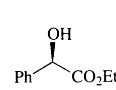
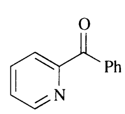
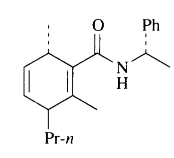
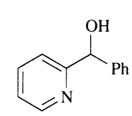
Ketone	Chiral Reagent	Product(s), Yield(s) (%), and ee			Refs.
C_6					
			(100)	51%	262
C_7					
	"		(95)	99%	262
	"		(100)	62%	262
	159	"	(67)	90%	263
C_8					
	 , PhMgBr		(90)	67%	317
		 Ar / (%) / ee: Ph 60 70%; m-BrC_6H_4 77 89%			262
		 Ar / (%) / ee: p-ClC_6H_4 75 95%; m-$O_2NC_6H_4$ 85 99%			262
C_9					
			(100)	97%	262
		"	(100)	95%	262
			(100)	98%	262
	"		(74)	95%	262
C_{10}					
	 , $Mg(ClO_4)_2$		(84)	83%	261
	159	"	(67)	98%	263

TABLE VIII. ENANTIOSELECTIVE REDUCTION OF KETONES WITH CHIRAL DIHYDROPYRIDINE REAGENTS (*Continued*)

Ketone	Chiral Reagent	Product(s), Yield(s) (%), and ee			Refs.
C_{12}					
			(97)	77%	262
	159	"	(72)	100%	263

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The Retro–Diels–Alder Reaction Part I. C - C Dienophiles

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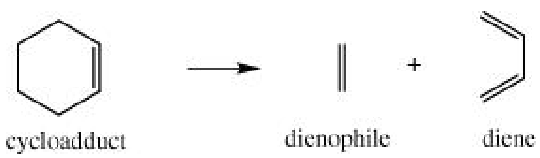
1. Introduction

1.1.1. Definition

The Diels–Alder ("DA") reaction is so familiar to organic chemists that the retro-Diels–Alder or retro-diene reaction (hereafter "rDA") requires no conceptual introduction. However, a working definition is needed to indicate the coverage of this review. The intent is to include all reported examples of the general skeletal process:



Any of the atoms in the starting material (cycloadduct) may be carbon or heteroatom, and substituents on all positions are allowed. In addition, any bond order available to the element in any oxidation state is included, as well as bonding to non-nearest neighbor atoms (bicyclics, etc.).

The volume of literature required separation of this review into two parts. Part I covers all expelled C–C dienophiles, i.e. those reactions that generate a new carbon-carbon double or triple bond in the dienophile that is formed. Part II, to appear later, covers those expelled dienophiles in which one or both atoms is a heteroatom.

1.1.2. Topics Omitted

Certain specific topics are intentionally omitted. These are:

- rDA reactions invoked under mass spectral conditions. Numerous references to this topic exist, but very few are of interest to preparative organic chemistry.
- rDA reactions of polymeric substrates. This important topic is not easily accommodated by the tabular format of this series, and the products are often not well-characterized.
- electrocyclic processes, some of which are arguably very similar to rDA reactions. These are not addressed unless needed for clarification of an rDA

sequence. The reaction most similar to an rDA reaction is the cyclohexadiene— hexatriene rearrangement and its heteroatom equivalents, but analogies can be drawn for any six-electron process. Cheletropic reactions (e.g., expulsion of CO or SO_2) are not covered unless occurring in a sequence involving an rDA step, even though some earlier writers have described cheletropic processes as rDA reactions. In the discussion of mechanism, attention is paid to Cope rearrangements in which the product could in principle also arise by rDA/DA sequences (the "Woodward–Katz rearrangement").

- thorough discussion of homo-rDA reactions. No effort was made to do an exhaustive search of homo-rDA reactions, but several are included, particularly if they lead to useful reactivity comparisons.

1.1.3. Literature Coverage

CAS-Online searches resulted in ca. 1,300 references, of which ca. 900 proved pertinent to the rDA topic as defined and delimited above. Active literature searching was halted in April 1995, but occasional more recent articles are included.

Over 2,500 pertinent references were eventually found. Most were obtained by perusal of primary literature (articles) and secondary sources (books and reviews). Computer based search success was limited mainly by the failure of authors or abstractors to key-word this topic, an especially common occurrence when the expelled dienophile was a simple substance such as N_2 or CO_2. Overall, approximately 3,500 books, chapters, reviews, articles, and abstracts were consulted in an effort to make this review as comprehensive as possible. This was done with the certainty that some pertinent literature would be missed, tempered by the view that these omissions are probably also lost to any future rational search method.

Many secondary sources proved valuable not only for in-depth discussion of certain rDA reaction types, but also for providing comparisons with related topics. To assist the reader, these secondary sources are referenced (alphabetically by first author within broad subject areas) with a title or brief note on the topic(s) addressed. The first group lists earlier reviews with primary focus on rDA reactions, (1-7) followed by items of Historical/General Interest, (8-13) reviews that deal with Experimental Methods, (14-23) DA reactions (general and specific), (24-62) reviews of Related Topics (these impinge in more or less significant ways on rDA reactions), (63-104) and general treatments of Theory and Mechanism. (105-117)

2. Mechanism

The general mechanistic questions that have arisen in the context of rDA reactions deal with (a) the timing of bond breaking (concerted vs. two-step processes); (b) the possibility of an intramolecular process leading to *endo/exo* interconversion, and (c) the relationship between certain Cope rearrangement and rDA/DA sequences that could in principle give the same products. Substituent effects, catalysis, and subtle bond orientation effects (118) continue to be foci of research efforts. The ultimate goal of mechanistic studies remains the ability to predict structure/reactivity relationships.

The wide range of conditions used, and the highly variable cycloadduct structures employed, make broad generalization about any single mechanism for rDA reactions hazardous. Some reactions are highly endothermic, while others are highly exothermic. Some occur at very low temperatures, and others require temperatures at the other extreme of a range that exceeds 1,000°. The energy needed to effect rDA reactions has been introduced by every conceivable means, thermal (heating neat or in solution, flash vacuum pyrolysis, shock tube, etc.), photochemical (direct, triplet-sensitized, pulsed laser), and gamma-radiation. The effects of sonication and high pressures have been explored, as well as the role of acids (both Lewis and protic) and bases.

Stereochemistry is typically of major interest in DA reactions. Less attention has been paid to this aspect of rDA reactions, the obvious reason being that the number of stereochemical relationships is diminished in this direction. The basic stereochemical features of thermal rDA reactions are those expected from consideration of similar DA reactions; i.e., *cis* substituents in the cycloadduct become *Z* in the dienophile, and the usual stereochemical features in the diene geometry are preserved. No exceptions to these generalizations have been noted in the preparation of this review. Instances of incomplete specificity are not uncommon, but may be due to unrelated isomerization of starting material or product. Several reactions that exhibit the expected stereochemistry are shown in the tables.

The stereochemical outcome is less obvious in “photochemical” rDA reactions, since the electronic spin state of the reactive intermediate is typically unknown. (119) It appears that UV may serve simply as a way to introduce the energy needed for “thermal” cleavage, or it may cause reaction via an excited electronic state, with loss of stereochemistry; isomerization of products is of course also a source of difficulty in these experiments.

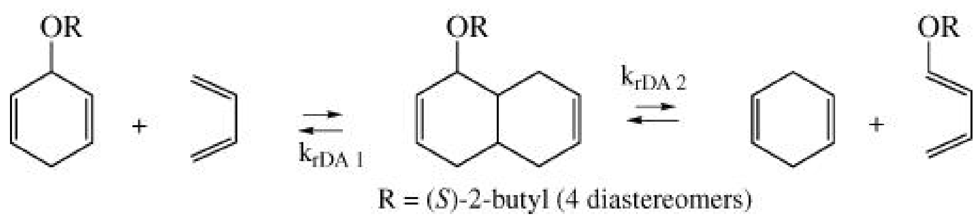
Failed reactions can be mechanistically informative. Thus, the *trans* fused adduct does not give rDA products, presumably owing to the strain inherent in the (*E*)-cyclopentene that would be formed in a stereospecific rDA process. Instead, a [1, 3] rearrangement takes place. (120)

Endo/exo preference studies have long been a staple of DA reactions. Usually the kinetically controlled product ratio is of interest, although equilibration may also be of concern. In contrast to DA reactions, little is known about this stereochemical feature in rDA reactions. Only a few isolated systems have been studied in sufficient detail to provide relative rates for rDA reactions of *endo/exo* isomers. It is important to recognize that the rates of equilibration of cycloadduct isomers can provide evidence for the rate of rDA reaction of only one isomer, and the identity of this isomer is not uniquely provided by this information.

Theorists have, for obvious reasons, focused mainly on the simpler all-carbon systems in addressing DA(rDA) mechanisms. Calculations of transition state geometries and energies often start with cycloadduct structures, since there is general agreement that the transition state of a typical DA reaction more closely resembles product (cycloadduct) than the starting diene/dienophile. The “trajectory” examined is often that of the rDA reaction from cycloadduct to the common transition state, even when primary interest is ostensibly the DA direction.

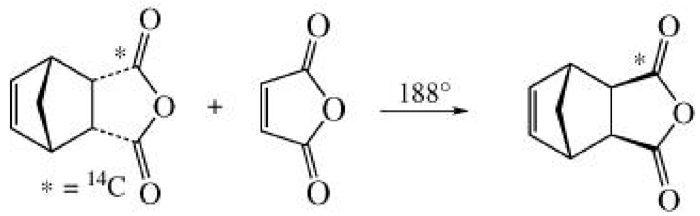
Computational methods as applied to the simplest DA reaction, between ethylene and butadiene, have evolved substantially in the last two decades, leading to general acceptance that the transition state is symmetrical, as expected for a concerted process. (121-124) Early MNDO calculations suggested otherwise, (125, 126) but these are no longer considered realistic. The introduction of a substituent adds considerable complexity to the calculation and to the range of transition state features that may be favored. (122-124) Groups that stabilize free radical centers will enhance dissymmetry, with the extreme favoring a diradical intermediate (stepwise mechanism).

Various specific features of DA (and by inference rDA) reaction mechanism have been addressed by theorists. An MNDO/AM1 approach led to the conclusion that steric effects are at least as important as secondary orbital interactions in determining *endo/exo* ratios. (127) Solvent effects on DA reactions have been explored by an ab initio/SCF method, again working backward from cycloadduct to the transition state. (128) Substituent effects are addressed in a classical HMO study on rDA and other pericyclic reactions. (129) The AM1 approach was shown to give a reasonable qualitative correlation of substituent effects with experimental rDA data, with some exceptions. (130) The AM1 method also indicated that the overall equilibrium (between educts) would favor the vinyl ether product. Although this result is in accord with recognized thermodynamic factors, the calculations also indicated that $k_{rDA2} > k_{rDA1}$, a more subtle point. (131)

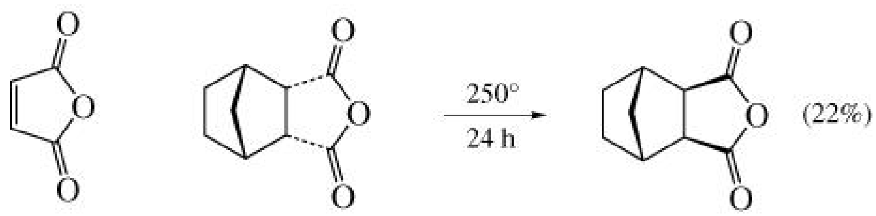


Maleic anhydride (MA) adducts have figured importantly in the study of rDA mechanisms. Already by 1936 cyclopentadiene adduct(s) (*endo/exo* unknown) had been isolated and shown to dissociate into educts on heating. (132) The isolation of diene/dienophile is clearly strong evidence for a dissociative rDA mechanism. Later, when *endo/exo* stereochemical relationships were better understood, questions arose about the possibility of interconversion by an intramolecular pathway. The inability to detect educts in the *endo/exo* interconversion of dimethylfulvene-MA adducts led to the suggestion that a non-dissociative mechanism was operative. (133) It is clear, however, that an equilibrium strongly favoring cycloadducts may make detection of educts infeasible, and this seems the more likely explanation in all instances in which intramolecular mechanisms have been proposed based on “negative” detection results.

This rationale cannot explain the unexpected results of an experiment designed to test this question through the use of radiolabeled adduct. The ^{14}C labeled *endo* isomer was heated in the presence of unlabeled MA. Analysis of the *exo* isomer isolated from this experiment indicated that it contained more ^{14}C than predicted by complete dissociation with scrambling of MA (although some label had been lost, also ruling out an exclusive intramolecular pathway). (134)



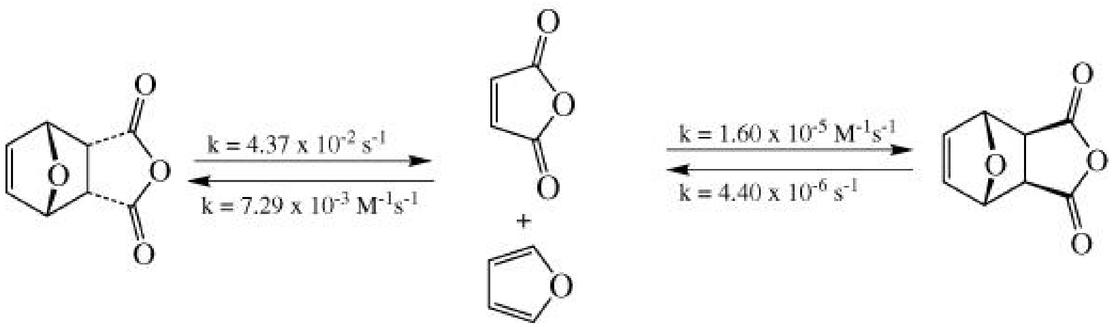
This intriguing result set off a flurry of activity, including efforts to find other examples of (apparent) intramolecular *endo/exo* interconversion. All concluded with support for fully dissociative rDA reactions. What then is the reason for the anomalous result described above? One possibility is hydrolysis followed by double epimerization and closure to the exo anhydride. Lending credibility to this suggestion, *endo/exo* isomerization also occurs with the saturated analog, albeit at higher temperature. (135) Presumably rDA reactions of any sort are ruled out in this system.



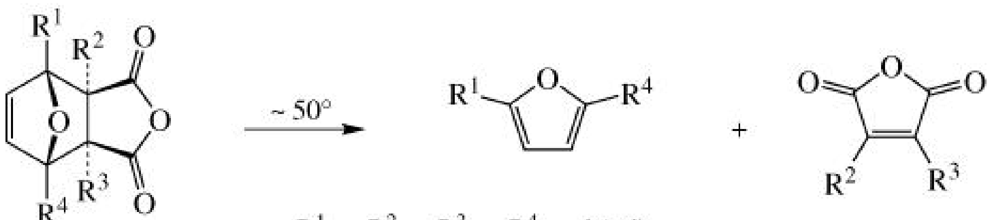
The DA reaction of cyclopentadiene (CP) with MA occurs readily near room temperature, with kinetically favored formation of *endo* isomer. The reaction is exothermic by ~25 kcal/mol. (136) The cycloadduct is representative of many substrates that undergo dissociative rDA reaction without easily detected educts. Interconversion to the *exo* isomer at reasonable rates requires temperatures ³150°. (137)

The furan-MA system has also provided important mechanistic information, after a somewhat hesitant start. Woodward corrected earlier *endo/exo* assignments, noted that the DA reactions are readily reversible, and showed that the *exo* isomer is favored at equilibrium. (138) Failure to observe educts when solid *endo* isomer isomerized to *exo* on heating led to the suggestion that an intramolecular pathway might be available, (139) but all later work shows that this suggestion is untenable. Although the *endo* adduct can be maintained as a solid for prolonged periods, dissolution in acetone at room temperature effects rapid (5 minutes) dissociation to furan and MA. (140) The *exo* isomer is only slightly dissociated under these conditions. (140)

This system is one of the very few that has been fully characterized kinetically at a single temperature. The rate constants for both DA reactions and both rDA reactions in acetonitrile at 40° are shown. (141) These data quantify earlier observations in a striking way. The *endo* isomer is formed a remarkable 455 times faster than *exo*, but the *endo* adduct is less stable than either the educts (if dilute) or the *exo* adduct. The latter becomes the thermodynamic sink under typical reaction conditions.

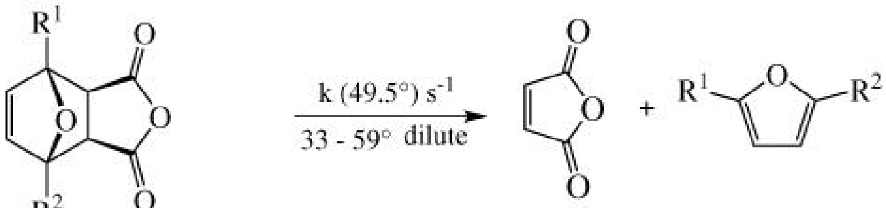


Deuterium isotope effects were measured in a series of experiments involving the *exo* adduct of 2-methylfuran and MA. The results were interpreted as favoring a concerted rDA mechanism. (142)



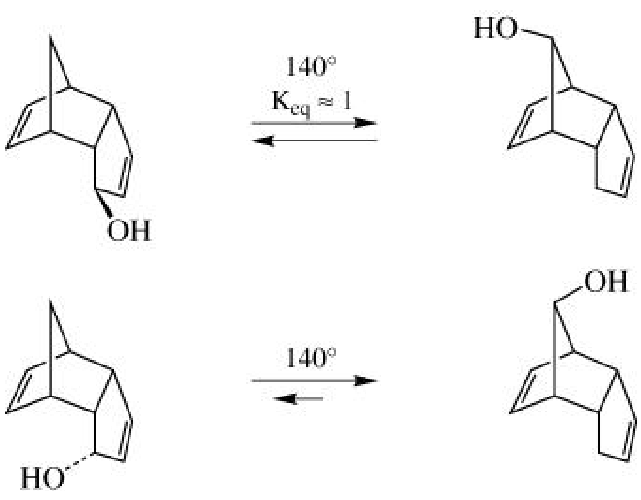
	R^1	R^2	R^3	R^4	k(rel)
I	H	H	H	Me	1
II	H	D	D	Me	0.867
III	D	H	H	Me	0.932
IV	H	D	H	Me	k(**IV**)/ k(**V**) = 1.00
V	H	H	D	Me	
VI	H	H	H	CD_3	0.971

The use of the 2-methylfuran adduct makes this rDA reaction inherently unsymmetrical, but the perturbation appears to be relatively minor. Rate constants and activation parameters for the non-, mono-, and dimethylated derivatives have also been reported. (143) Although two of the derivatives show the low to slightly negative $\triangle S^{\#}$ terms that are typical of other rDA reactions, the monomethyl derivative appears somewhat unusual in both rate and activation parameters, possibly owing to a consistent error leading to “compensating” activation parameters. Clearly methyl groups do not have a major effect on the rates of these rDA reactions. (*All energy terms are expressed in kcal/mol; entropy in cal/mol.deg.*)



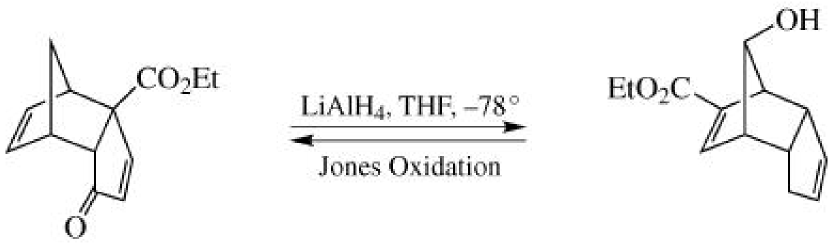
R^1	R^2	k x 10^5	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
H	H	8.81	25.0	0.2
H	Me	6.92	20.8	–8.6
Me	Me	16.4	20.3	–2.2

In 1959 Woodward and Katz published a fascinating and somewhat controversial paper entitled “The Mechanism of the DA Reaction”, in which the stereospecific (and therefore intramolecular) interconversions shown below are described. (144)



Woodward and Katz noted that these reactions constituted “special cases of the Cope rearrangement”, but pointed out that certain similarities existed with the mechanism of DA/rDA reactions, and further argued that the DA reaction general mechanism must involve a stepwise process. (144) Whether or not there is a common structural feature in the energy surfaces of DA(rDA) reactions and Cope rearrangements remains a valid question, (113, 114) although efforts to demonstrate this point have to date given negative answers. Both theory and experiment support the view that simple DA(rDA) reactions are concerted (nonsynchronous) processes, as noted above. The “Woodward–Katz” variants of Cope rearrangements must nonetheless be considered in the context of rDA reactions, since they constitute in all instances competing (and usually winning) reactions that might otherwise have taken dissociative rDA pathways. The Cope alternative must always be kept in mind when dealing with materials encompassing the fixed (or accessible) 1,5-diene stereochemistry that favors [3,3] rearrangement, characteristic of *endo* dicyclopentadiene.

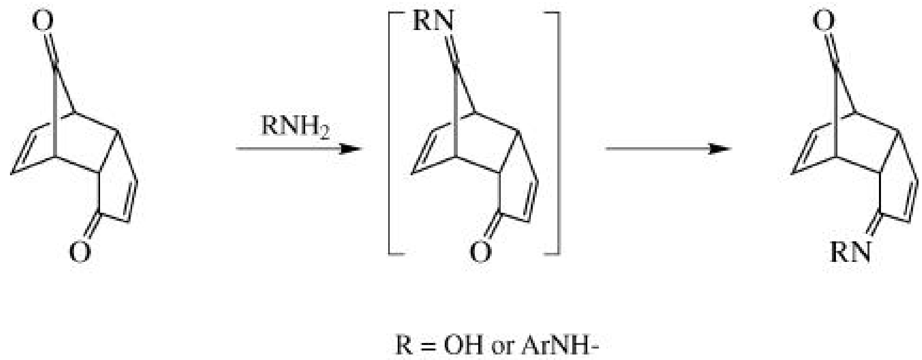
An especially interesting “oxy-Cope” variant that occurs under quite mild conditions has recently been described. (145)



This “redox” equilibrium illustrates the general conclusion that if only one carbonyl group is incorporated, it has a strong preference for the fused ring, whereas the reduced carbinol will generally prefer the bridgehead position to the (hindered) endo site. In the example shown, conjugation of the ester function also plays a role. The left-hand structure is strongly favored in the oxidized form, while the right-hand structure is strongly favored in the reduced form.

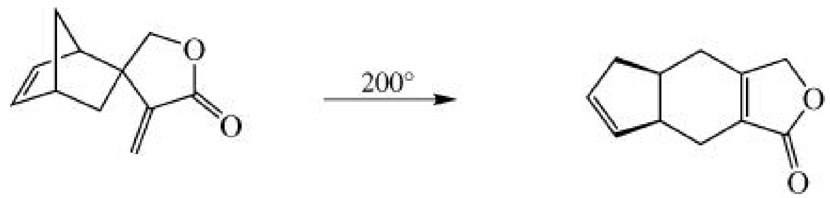
The preference for the fused-ring carbonyl isomer is also observed in the parent monoketo structure; this bridge-to-fused ring transformation occurs with acid catalysis at ambient temperature. (146) Similar observations have been made with a partially chlorinated analog. (147)

The *endo* dimer of cyclopentadienone exhibits related but less obvious behavior when converted to monoimine or oxime. The bridging carbonyl is expected to be the more reactive toward nucleophilic reagents; rearrangement of the presumed initially formed product to fused ring imine must then be rapid. (148, 149)

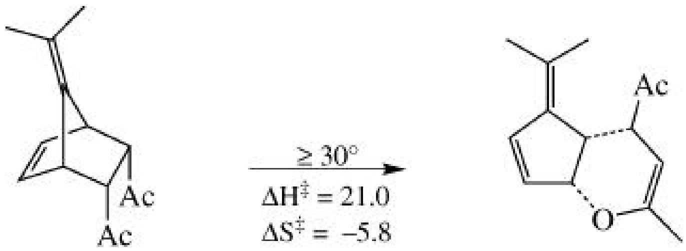


Other skeletal *endo* dicyclopentadiene [3,3] rearrangements that have been described are those of the (Me)CP adduct (150) and the (Cl_6)CP adduct, (151) both with CP as diene. Tropone (as dienophile) adducts of CP, (152) dimethylfulvene, (153) and a substituted cyclopentadienone undergo analogous Cope rearrangements, (154, 155) although products attributable to the rDA reaction are also observed in some instances.

The complete tricyclic structure obviously need not be present for related Cope rearrangements to take place. Although the temperature used in the next example is in the range needed for rDA reaction, the isomerization is thought to occur as a [3,3] intramolecular reaction. (156)

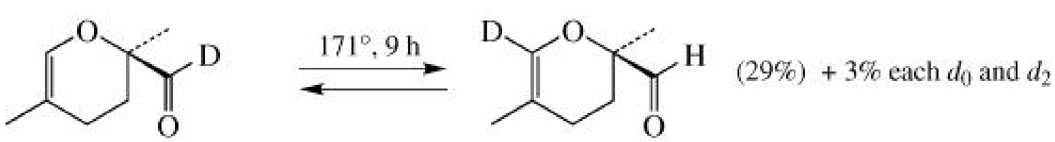


The *endo cis*-diacetyl adduct of dimethylfulvene undergoes [3,3] rearrangement near room temperature. The *trans* adduct is reported to be more robust, and gives rDA reaction instead. (157)



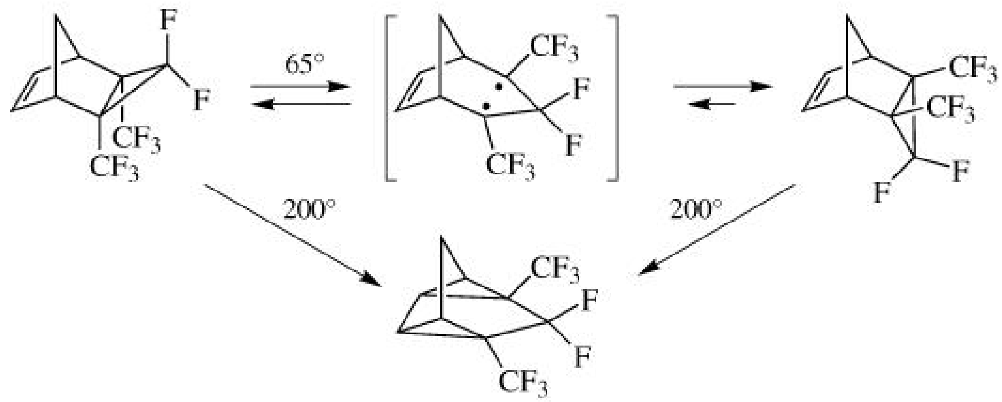
Several substrates that contain embedded heterodienophiles also exhibit a tendency for Cope- or Claisen-like rearrangement rather than rDA reaction. Azodicarboxylate and related *N*-acyl adducts of CP and substituted cyclopentadienones provide well-documented examples. (158-161) *N*-Acylnitroso derivatives behave similarly; (162, 163) in both substrate types it is assumed that the carbonyl group either exists in or can readily attain the *endo* geometry needed for rearrangement. A related rearrangement is observed for an *endo* sulfoxide at 40°, whereas the *exo* isomer is unchanged up to 120°; in this case the oxygen lone pair serves in place of the double bond. (164)

An attempt to explore the energy surface question was made with a deuterated methacrolein DA dimer. After partial reaction (71% of monodeuterated unchanged starting material; note that forward and reverse reactions are identical by symmetry, neglecting isotope effects), the major product (29% of the monodeuterated material) was that derived from intramolecular rearrangement, but smaller amounts of products arising from dissociation (rDA) and subsequent DA reaction were also detected, and some methacrolein had distilled away. Rate constants were calculated for the intramolecular ($k = 3.0 \times 10^{-5}\ s^{-1}$) and rDA reactions ($k = 8.6 \times 10^{-6}\ s^{-1}$). Clearly similar activation energies are involved, although commonality of the energy surface is not proved. (165)

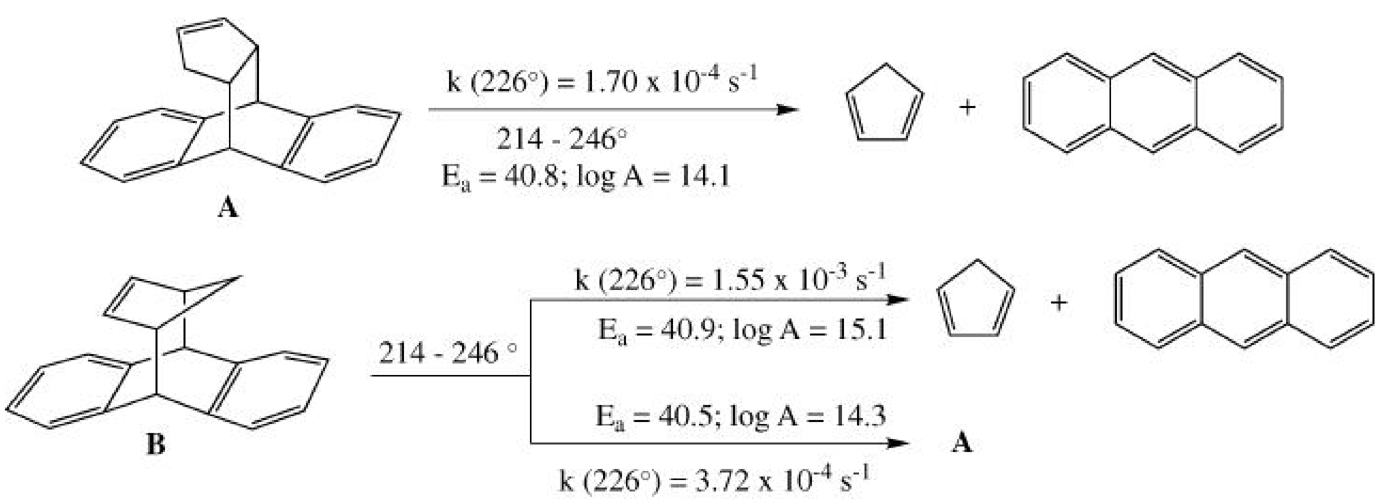


The present state of information on the possible relationship between Cope and rDA/DA mechanisms would likely not change earlier views that these processes are unrelated, (166) or simply that no relationship has been demonstrated. (114)

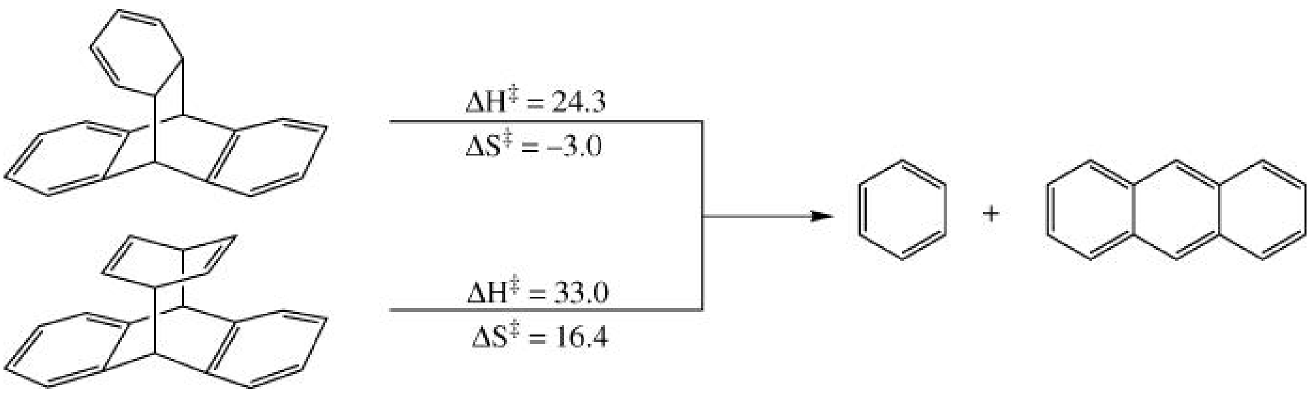
Unusual non-rDA *endo/exo* interconversions have been reported for some fluorinated cyclopropene-CP adducts. Diradical intermediates are proposed for these facile reactions, as shown for one system. Interestingly, conversion to the tetracyclic isomer requires much higher temperature. (167, 168)



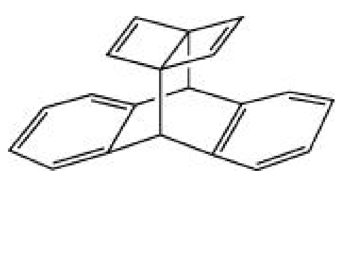
One might expect symmetry-allowed concerted reactions to proceed more readily than related symmetry-forbidden (and therefore stepwise) processes, but this need not be the case. An example is found with the anthracene-CP adducts **A** and **B**. Although the activation parameters for all three pathways are similar, the rate constants show that the “allowed?” rDA reaction of **A** is slower than scission of the [4 + 4] adduct **B**, which is believed to generate a diradical intermediate that subsequently dissociates and rearranges to form **A**. (169)



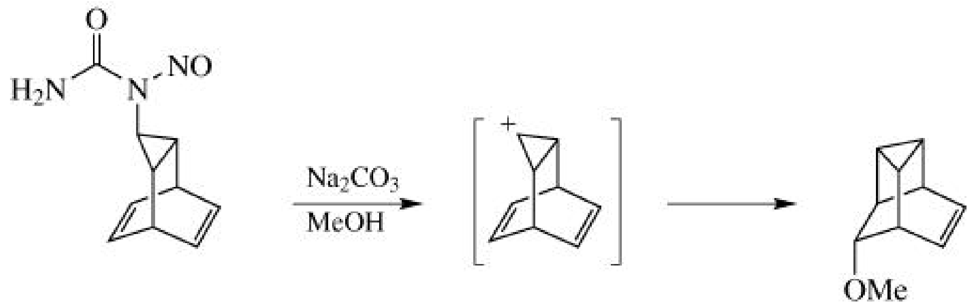
On the other hand, “normal” behavior is shown by the [4 + 2] and [4 + 4] isomers that dissociate to form benzene and anthracene. The rDA reaction is substantially favored by the $\triangle H^{\ddagger}$ term, while exhibiting a typically low (and not uncommonly negative) $\triangle S^{\ddagger}$. Note that the stepwise r[4 + 4] process will, because of the more positive $\triangle S^{\ddagger}$, become increasingly favored at higher temperatures (this reaction occurs readily at 80°). (170)



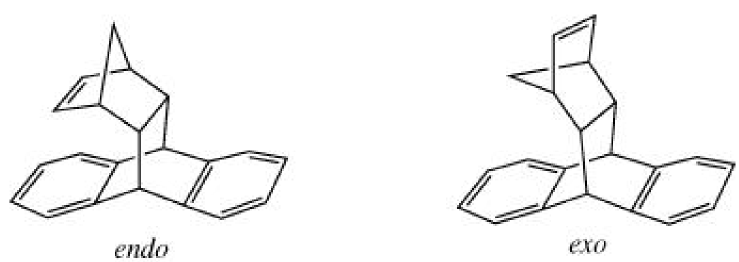
As later discussion will demonstrate, the thermodynamic stability of a product may play a major role in rDA reactions, but many highly reactive and “unstable” materials have been generated using this method, and indeed this is one of its chief values. Substrates of appropriate structure that fail to give rDA reactions thus merit attention. Intervention of more facile (e.g., Cope) reactions may occur, but some interesting substrates are simply reluctant to give rDA reactions. One is noted here, and others will be pointed out in later sections. Considerable effort went into the preparation of the Dewar benzene-anthracene adduct, which proved to be remarkably thermally stable up to 500°; if Dewar benzene was formed at higher temperatures, it did not survive. (171)



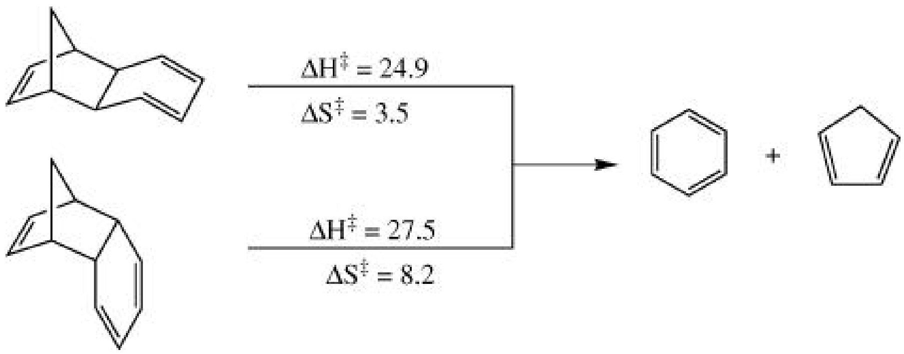
On the other end of the “stability” argument, it was reasoned that the prospective formation of two Hueckel aromatics, benzene and cyclopropenium ion, should make for a very favorable rDA reaction. However, a solvent trapping process intervened, as illustrated. (172)



The effects of stereochemistry on rDA reaction rates can be subtle, and this topic has not been adequately studied. Additional examples will be discussed in the context of different substrate classes in the Scope and Limitations section, but the *endo* and *exo* isomers shown below illustrate the point. Note that these materials have two potential rDA pathways available, one leading to CP + dibenzbarrelene, and the other anthracene + norbornadiene. The *exo* isomer decomposes by both routes at a temperature around 400°, conditions under which the *endo* isomer is reported to be stable. (173) The isomeric difference is not easily rationalized, and the temperature needed is higher than one might have predicted, especially for expulsion of CP.

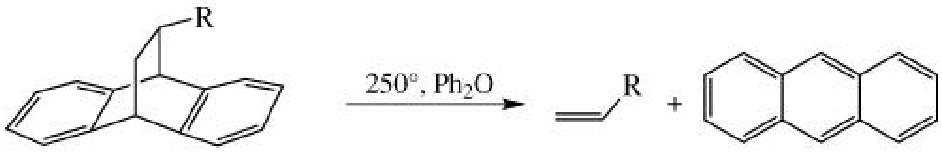


A more definitive example of an *exo* isomer being more reactive in the rDA reaction is found in the work of Wege. (174) Both isomers decompose to benzene and CP with rates measured in the 40–60° range, giving the activation parameters shown. To provide additional context, at 60° k_{exo}/k_{endo} = 4.35.



Endo and *exo* isomers are defined by more or less arbitrary rules of nomenclature, and there is no a priori reason to expect a general correlation with rDA reactivity. Indeed, as already seen from comparison of the MA-furan system and the present example, no correlation exists. Put another way, there does not appear to be an rDA analog of the “Alder rule” for *endo* selectivity in DA reactions.

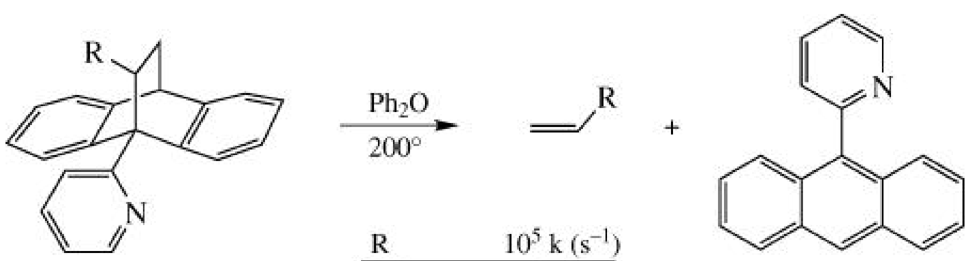
Surprisingly few quantitative studies of substituent effects have been carried out, although there are several qualitative observations that bear on this topic. In benchmark studies, a broad array of substituents on both dienophile and diene was explored. (175, 176) Anthracene derivatives were employed, and consequently the reactions required relatively high temperatures. Over 20 groups were included, as monosubstituted ethylene dienophiles. From a DA perspective, anthracene may be regarded as a modestly reactive (similar to butadiene) HOMO diene, and its reactions are typically more rapid with electron poor LUMO dienophiles. If substituent effects on bond strengths were negligible (clearly an oversimplification), the rDA reaction rates should parallel the DA rates (easy on, easy off). The data show a general trend in this direction, but there are some notable exceptions including the most reactive rDA entry, R = $N(Me)_2$. The authors attributed the exceptional effects to resonance stabilization of the transition state. Among the interesting points, the small (and even negative) effects of alkyl substituents, and the modest range of reactivity associated with traditional electron-releasing and withdrawing substituents (compare R = OMe and R = CN, for example) are noteworthy. Relative rates (rounded) are displayed below the reaction.



R	k_{rel}	R	k_{rel}
OAc	0.30	NO_2	17
t-Bu	0.73	$CONH_2$	33
i-Pr	0.80	CO_2Me	57
Et	0.90	CN	76
Me	0.94	NH_2	83
H	1*	Ph	123
OH	1.3	CO_2H	139
OMe	2.2	Ac	179
OTMS	2.3	CHO	251
NHAc	14	NH_3^+	1680
TMS	16	NMe_2	2480

$*k = 1.21 \times 10^{-5} s^{-1}$

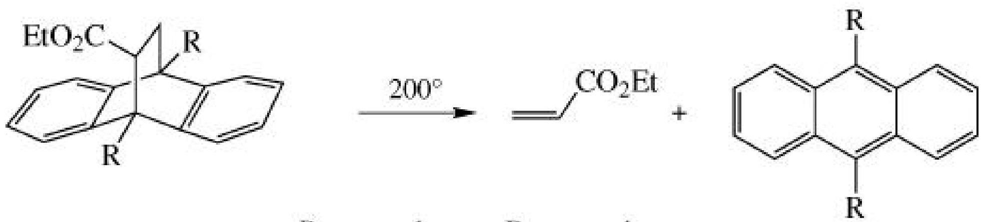
A more limited study of four traditional LUMO dienophiles and a pyridyl substituted anthracene is also shown. These reactions were done at a somewhat lower temperature (200°), introducing another variable; the small differences in rate do not exactly parallel those reported above, but the similarities are perhaps more notable than the differences, given the unsymmetrical diene component. (177)



R	10^5 k (s^{-1})
CN	1.5
CO_2Et	5.2
$CONH_2$	6.1
CO_2H	17.7

The bane of mechanistic studies is the inability to affect only a single variable in a reaction pathway by introduction of a substituent. Even the simple anthracene derivatives (except R = H) are unsymmetrical, and the substituent may affect the asynchronicity of bond-breaking.

A related study of substituents on the diene component also covers a broad range of functional groups. This work utilizes ethyl acrylate as the common dienophile, with the diene substituents introduced at both the 9- and 10-positions of anthracene. An anomalous effect for R = OH was originally reported, (178) but corrected in a later summation. (175)

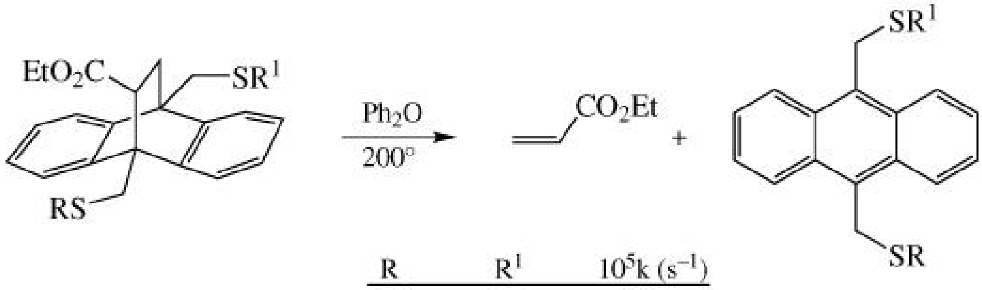


R	k_{rel}	R	k_{rel}
NH_2	2300	Me	2.3
OH	365	Ac	1.9
OTMS	264	OAc	1.9
NMe_2	139	H	1*
OPh	115	Cl	0.8
OMe	40	I	0.8
SMe	20	Br	0.5
Et	20	CO_2Me	0.24
i-Pr	7.9	F	0.2
CHO	4.8	NO_2	0.02
TMS	2.7		

*$k = 1.772 \times 10^{-5} s^{-1}$

The double substitution introduces the question of whether the numbers have meaning in terms of a single substituent effect, the problem again being due to the potential for asynchronous bond breaking associated with the use of an unsymmetrical dienophile. It would be useful to have data for analogous reactions with, e.g., MA as the embedded dienophile. Lacking such information, any comparisons must be made with caution; to the extent that such comparisons are valid, it appears that the effect of 9,10-dimethyl substitution is much smaller on rDA than on DA reactions. This diene continues to hold the record as the most reactive uncharged anthracene in DA reaction with MA, under conditions where 9-methoxyanthracene is (slightly) more, and 9,10-dimethoxyanthracene (slightly) less reactive than the unsubstituted parent. (113)

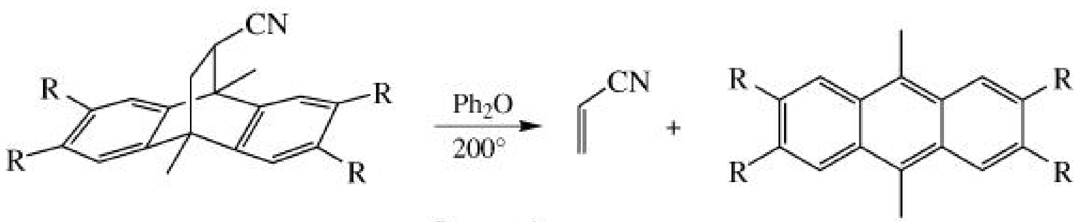
An interesting extension of the 9,10-dimethyl system was made with sulfur-substituted derivatives, all of which were more reactive (factors of 6–12) than the dialkylated model. (175)



R	R^1	10^5k (s^{-1})
Me	Me	26.4
t-Bu	*t*-Bu	48.4
$–(CH_2)_8^–$		40.3
$–(CH_2)_{10}^–$		40.3

Substituents at other sites on the anthracene ring have been little explored. Oxy substituents at remote sites modestly enhance the rates of rDA reaction. (175, 179)

Several additional examples of substituent effects are described in the context of particular dienophiles in the next section.



R	k_{rel}
H	1
OMe	14
*	19

* *o*-R,R = $–OSi(Bu\text{-}t)_2O^–$

3. Scope and Limitations

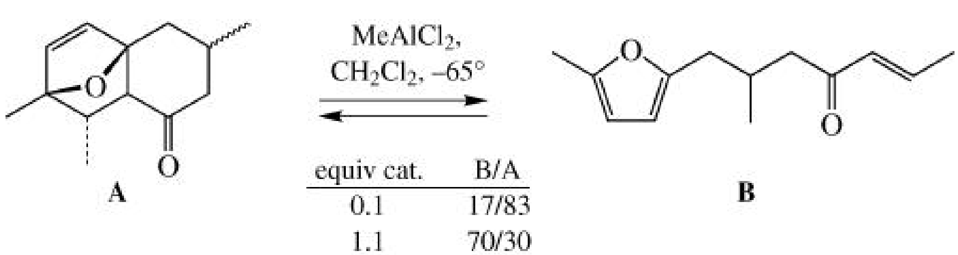
The DA reaction is clearly one of the most important and widely used of all processes in organic synthesis. Aside from the obvious relationship to the DA reaction based on microscopic reversibility, the rDA reaction has evolved into a powerful synthetic tool in its own right. It is either the method of choice, or the only known method, for preparing many reactive, strained, and metastable materials. Not surprisingly, the rDA reaction was included in early computerized retrosynthetic analysis schemes, (180) and more recently the DA/rDA set has been included in a “neural network” artificial intelligence training program. (181)

The scope of the rDA reaction is so broad that there are several approaches that may be taken in a review. Please refer to the “Organization of Tables” section for the main organizational features and common abbreviations, which will also be used in this section. Some general topics have been identified for discussion prior to focusing on individual dienophile types.

3.1. Acid Catalysis

Acids are frequently employed to speed DA reactions, often without comment on the possible effects on the reverse reaction. A true catalyst by definition will affect the rates of both forward and reverse reactions equally, without alteration of the equilibrium position. Among the small number (ca. 40) of clearly documented examples of acids affecting rDA reactions, very few represent true catalysis. In most instances, the acid is used in high concentration, often in excess of other reagents, and the effect on the equilibrium position is unknown.

Acids may thus influence both the rate and course of an rDA reaction, since the acid can remain complexed to the basic sites of both adducts and educts to differing degrees. A clear demonstration of this phenomenon is found in a study of the effect of Lewis acid concentration on the equilibrium position of an intramolecular DA/rDA pair. (182) A recent NMR study of competitive complexation provides support for this interpretation. (182a)



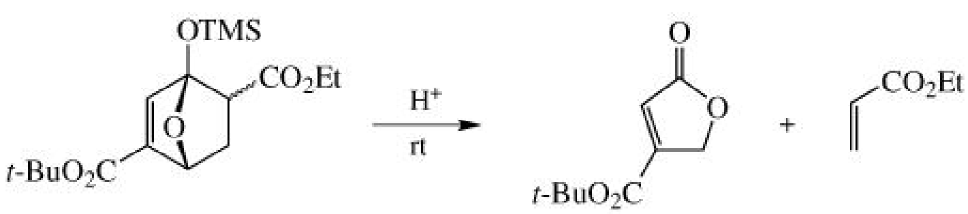
The facility of this equilibration is noteworthy. While intramolecularity is commonly expected to enhance DA reactions, it is perhaps less obvious that a dissociative process (rDA) can be similarly affected.

Both Lewis acids and protic acids have been used to enhance rDA rates. It is clear that the effect is associated with complexation or bonding to a basic site in one or the other of the embedded educts, usually the dienophile. A carbonyl oxygen, or nitrile or amine nitrogen, often provides the basic site. In the absence of basic sites, or with acids too weak to bond, no catalysis is expected; among the few experimental demonstrations of this feature, it has been shown that BCl_3 vapor does not affect the dissociation of cyclohexene into ethylene and butadiene. (183)

Chromatographic materials may enhance certain rDA reaction rates, sometimes with an effect on the equilibrium position. Examples include silica gel, (184-187) alumina, (188-191) and Florisil. (192) An alumina/silica mixture may play a role in the 450° rDA pyrolysis of dihydropyran. (193, 194)

Protic acids have been used with substrates such as amines and diazines that are reasonable Brönsted bases but which may interact weakly with some Lewis acids. The proton sources include trifluoroacetic acid (TFA), (195, 196) aqueous mineral acids, (197, 198) sulfonic acid exchange resins, (199) polyphosphoric acid, (200) and concentrated sulfuric acid. (201) Copper(II) sulfate has also been employed to effect the rDA expulsion of an imine dienophile. (199) A few examples of protic acid "catalysis" of rDA reactions of adducts containing only oxygen basic sites have also been reported. TFA and aqueous acid are thought to enhance expulsion of enones, (202, 203) and an ethereal oxygen may provide the basic site in the formal rDA reaction of a dihydrofuran derivative. (204)

An unusual example of indirect protic acid catalysis of an rDA reaction involves hydrolysis of a bridgehead — OTMS group to the bridgehead — OH, which then rapidly decomposes to educts. (205)



Numerous Lewis acids have been used to speed up rDA reactions, but very little comparative work has been done. It is therefore difficult to recommend conditions for a new substrate. For a particular reaction that generates an imine and a relatively simple diene, the order of reactivity ($TiCl_4$ > $AlCl_3$ > $ZrCl_4$ > Et_2AlCl > $BF_3 \cdot Et_2O$) was found. (206) Curiously, $AlCl_3$ has been little used to enhance rDA reactions, even though it appears that such "catalysis" may have been observed as early as 1931 by Clar. (207) Alkylaluminum analogs are more commonly employed, including $MeAlCl_2$, (208-210) Me_2AlCl, (211) $EtAlCl_2$, (208, 212) and Et_2AlCl. (213) Other Lewis acids that have been shown to expedite rDA reactions include ZnI_2, (214) $BF_3 \cdot Et_2O$, (215-219) and $LiClO_4$. (220)

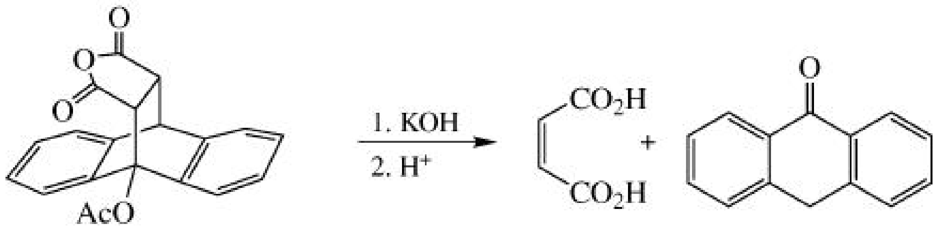
Modest yields of cyclopentenones (plus presumably CP) are formed when norbornadiene is treated with allylic bromides and CO in the presence of $Pd(PPh_3)_4$, and catalysis of an apparent rDA step appears probable. (221) Organometallics (Mn, Ir) are used to effect the rDA reactions of dithiin-1-oxides to form S_2O complexes and dienes. (222) The presence of $Co_2(CO)_8$ (³1 equiv) promotes both lower temperature and more selective rDA loss of acetylene from 1,2-annulated barrelene derivatives. (223) In contrast, Ru and Rh organometallic catalysts are used to enhance the yields of heptalenes at the expense of an rDA side-product (azulene diester) in reactions of azulenes with dimethyl acetylenedicarboxylate. (224)

All the reactions noted in this section are shown with added detail in the appropriate Tables. Wider use of acid-catalyzed (or acid-induced) rDA reactions is anticipated as these rate effects become more widely understood.

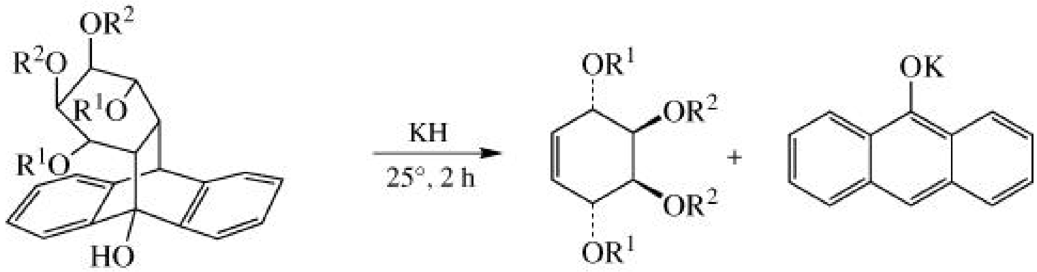
3.2. Base-Induced Reactions

Base *catalysis* of rDA reactions is unknown, but several examples of base-*induced* cycloreversions have been reported. In most instances the thermodynamic factors favoring the reaction include conversion of a stronger to a weaker base. Marked rate accelerations (relative to the neutral reaction) are also commonly observed, suggesting that entry onto the anionic energy surface may be generally beneficial. Relatively little use has been made of base-induced rDA reactions in multistep syntheses, owing at least in part to difficulties in preparing the appropriate cycloadducts.

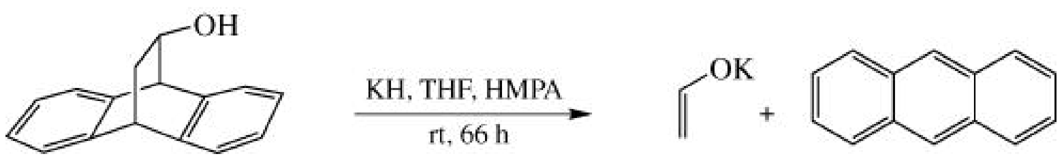
Oxyanion-induced reactions comprise the majority of base-induced rDA reactions. Although not widely recognized as such, the first example is evident in the 1934 report that an anthracene adduct, upon basic hydrolysis followed by acidification, gave only anthrone and maleic acid. (225)



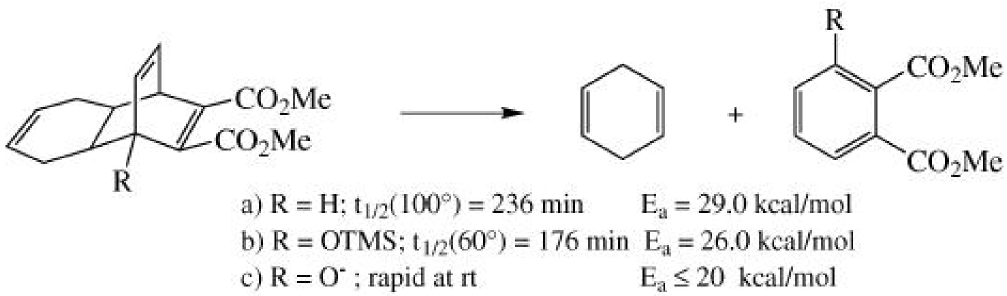
A more striking example of this reaction involves expulsion of the cyclohexene tetraol derivative; remarkably, this “poor” dienophile is formed at room temperature in this base-induced process. (226) This approach has recently been used to prepare a thermally unstable enediyne. (226a)



These processes are favored by the conversion of an alkoxide (alcohol pK_a » 18) to a phenoxide (phenol pK_a » 10). The formation of an enolate (enol pK_a » 10) is similarly favored, as shown in the next example. (227)

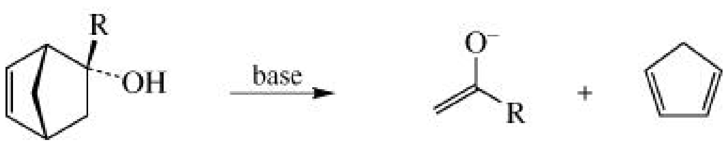


A useful comparison of bridgehead substituents shows that the uncharged $OSiMe_3$ group imparts appreciable rate enhancement, but an even larger effect is associated with the oxyanion, again showing the value of accessing the anionic energy surface. (228)

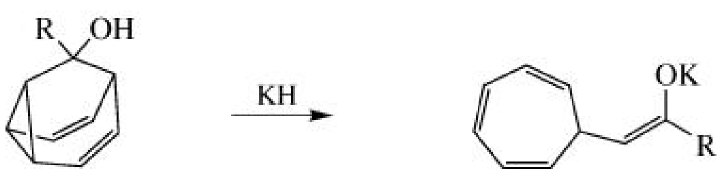


Gas-phase interaction of hydroxide ion with CP-cyclohexadienone adducts is thought to facilitate the rDA reaction, with formation of phenoxide. (229)

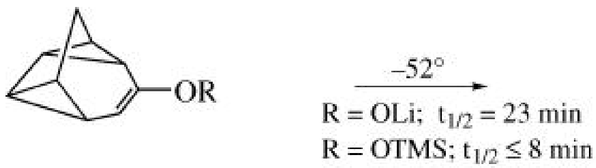
Some controversy has attended the report that *endo*-bicyclo[2.2.1]hept-5-en-2-ol (R = H) undergoes facile rDA reaction under more or less basic conditions. (230) In spite of criticism of this particular work, (227) it appears that the rDA reaction can occur in high yield when R =aryl. (231-233)



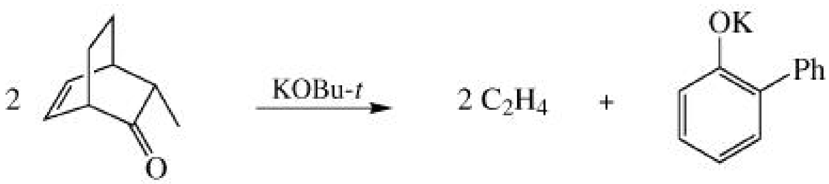
When R = alkyl, the same basic conditions lead to an intramolecular rearrangement product, resulting in the suggestion that the rDA reaction occurs by a stepwise mechanism. (231) A similar product is formed by a formal homo-rDA reaction from the semibullvalene derivative when R = aryl; for R = H or Me, no reaction is observed. (232)



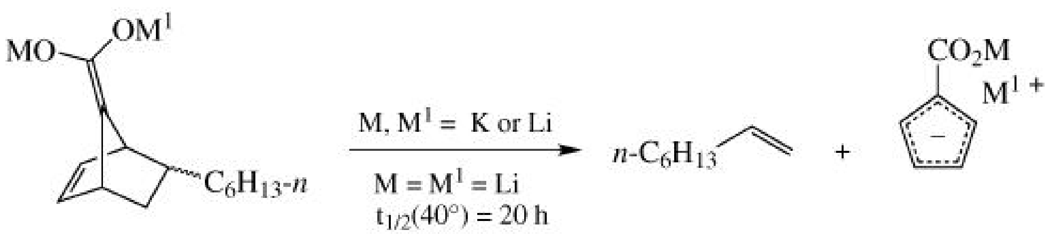
It is not clear that anionic effects are important in the next example, which involves conversion of one enol(ate) to another. In this system the $OSiMe_3$ derivative gives homo-rDA reaction more rapidly than the OLi analog. (234)



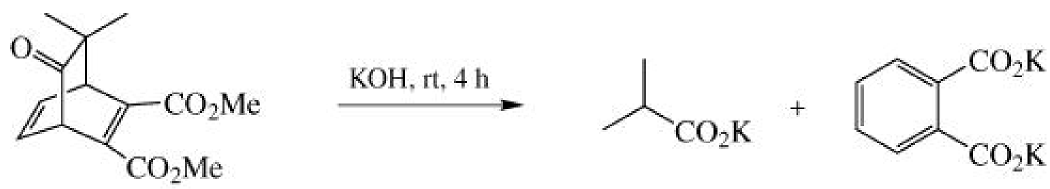
Bicyclo[2.2.2]octenone gives a mechanistically interesting reaction with base that leads to a biphenyl derivative. (235) The course of this reaction appears to be dictated by rapid initial aldol condensation, followed by successive rDA expulsions of ethylene.



The ratio of K/Li gegenions is proportional to the rate of rDA reaction of the dianion illustrated next. (236) This substrate bridges carboxylate (oxyanion) and cyclopentadienyl anion (Cp) chemistry. The ambient temperature rDA expulsion of the modest dienophile (octene) is noteworthy.

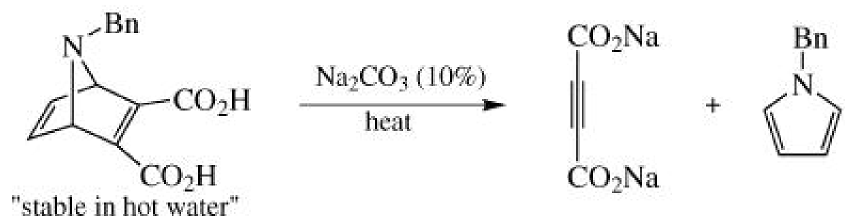


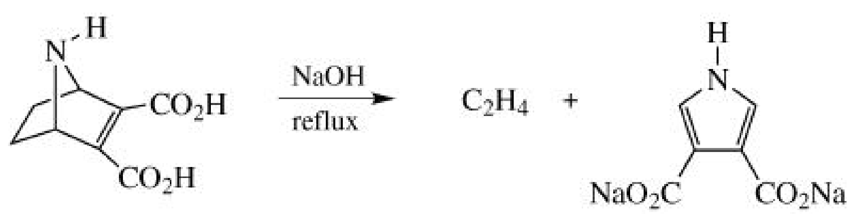
Bicyclo[2.2.2]octadienones are relatively unreactive thermally; the rDA expulsion of ketene(s) typically requires temperatures ³400° even when the “diene” that is formed is an aromatic. The high thermal barrier can be bypassed either photochemically (discussed later) or by base-induced reaction, which can be facile as indicated. (237)



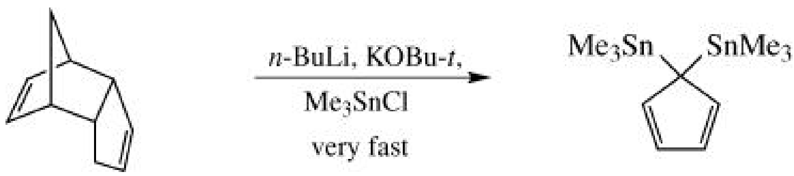
A related reaction with sodium hydride in dimethyl sulfoxide has been used to prepare polymethylated naphthalenes. (238)

To complete the survey of oxyanion-induced rDA reactions, some early pyrrole-forming work is noted. Although yields were not given, and not all products may have been accounted for or identified, it appears that conversion of the diacid to the dicarboxylate may increase rDA reactivity, and the order of dienophile expulsion: C_2H_4 > acetylene dicarboxylate > C_2H_2 is inferred. (239-241) Additional work on carboxylate salts is needed to determine the generality, if any, of rate effects on rDA reactions.

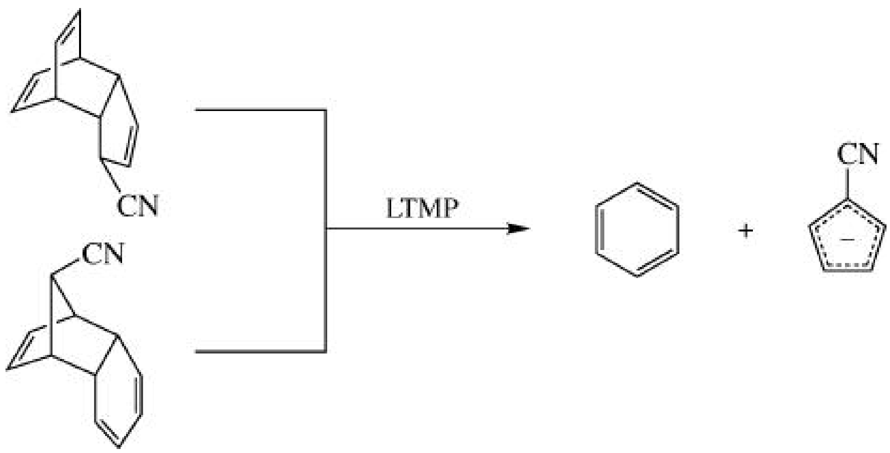




A second major class of base-induced rDA reactions involves generation of the resonance-stabilized (pK_a of CP » 15) anion of CP (Cp). Reaction may be initiated either by direct deprotonation with strong base, for example norbornadiene with amylsodium (leading to Cp + C_2H_2), (242) or as illustrated, *endo*-dicyclopentadiene with *n*-BuLi/KOBu-*t*. (243)

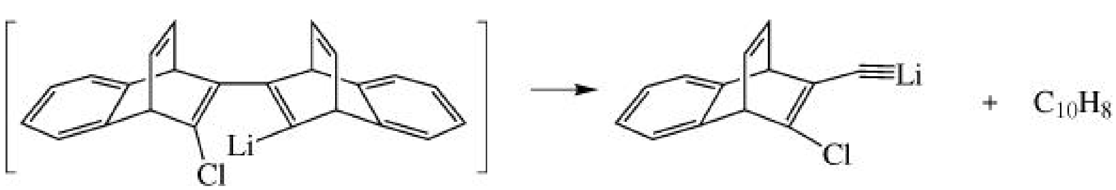


Substrates activated for deprotonation by electron-withdrawing groups have also been examined. (244) Benzene is readily formed, formally as either the diene or dienophile component, in base-induced reactions.

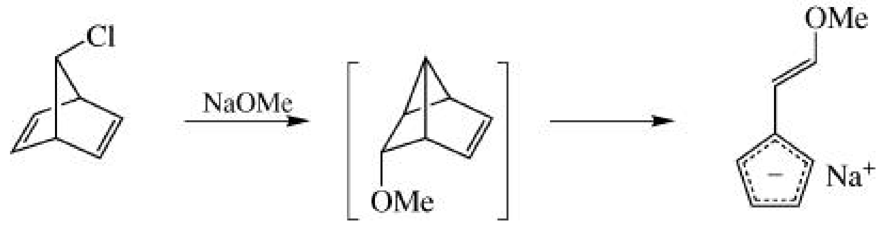


Other methods of forming reactive cycloadduct anions include treatment of a 7-chloronorbornene derivative with lithium metal, (245) metal/metal exchange (RLi/R¢Sn(Me)$_3$, (246) and reductive cleavage of methyl ethers by potassium (247) or sodium-potassium alloy. (248)

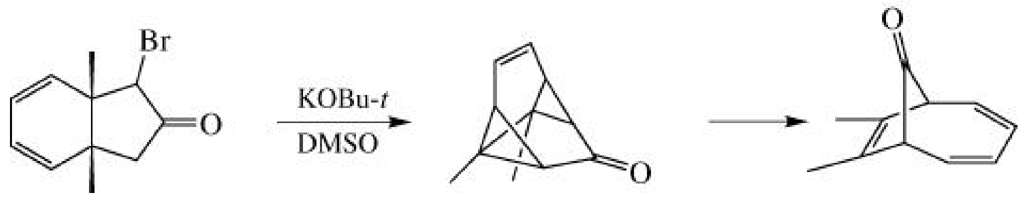
The rDA conversion of a vinyllithium to a lithioacetylide intermediate has been proposed in a sequence aimed at forming benzobarrelyne. (249)



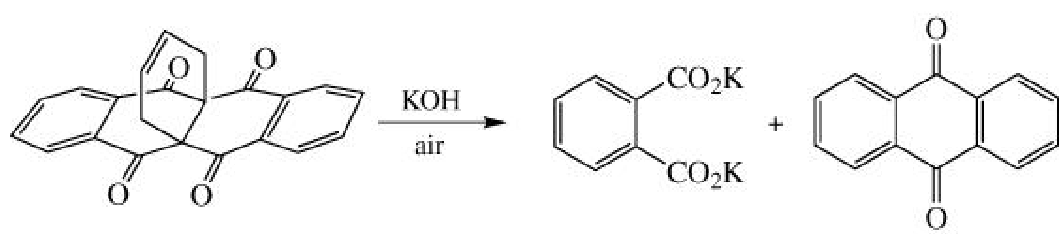
Some formal base-induced rDA reactions do not require pK_a arguments, and may instead be facilitated by relief of strain in intermediates. The reaction of 7-chloronorbornadiene with sodium methoxide provides one example. (250) A closely related solvolysis reaction that requires no active role for base has been described. (251)



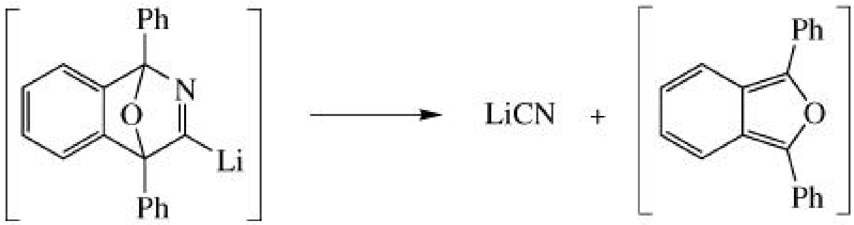
A homo-rDA step appears to be required for the skeletal rearrangement that accompanies base-induced HBr elimination reaction of a ketone, (252) and analogous reactions of tricyclic ketones and sulfones. (253, 254)



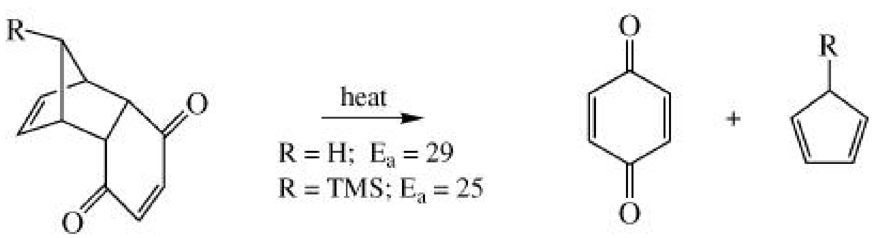
Another formal base-induced rDA reaction, although mechanistically likely to involve individual Haller-Bauer-like steps, was described many years ago by Fieser. (255) Under basic conditions air oxidation of the (presumed) initially formed dihydro product to form anthraquinone is observed.



Readily available 2,5-diphenyloxazole is rapidly deprotonated by lithium tetramethyl-piperidide (LTMP) (0°). The 4-lithiooxazole undergoes DA reaction (minor reaction) with benzyne to generate the intermediate depicted, which rapidly expells LiCN. (256) This rDA reaction is more rapid (qualitatively) than the loss of HCN from the conjugate acid. (257)



Alkali metal derivatives usually differ greatly in basicity and related reactivity, i.e. RK > RLi in many organic reactions. Formation of the anion (Cp) enhances rDA reactions as discussed above. Some covalent substituents can be regarded as having metalloid properties. The $(Me)_3Si$ group enhances rDA reactions. (258) The unsubstituted benzoquinone-CP adduct (presumably *endo*) was one of the earliest substrates subjected to rDA kinetic analysis, which gave E_a = 29 kcal/mol. (259) The $(Me)_3Si$ group reduces the activation energy to ~25 kcal/mol. (258)

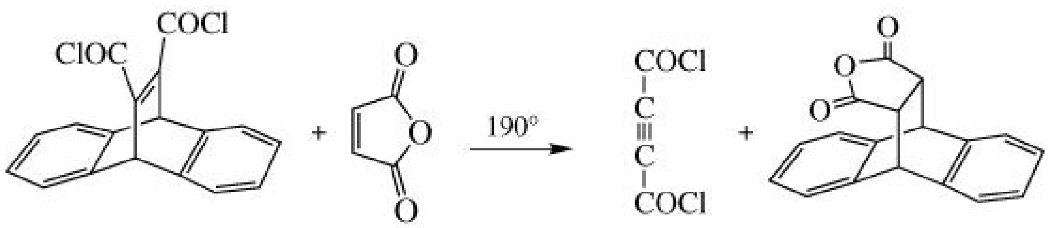


The role of R ¹ H in the facial selectivity of DA reactions of R-CP is an area of continuing interest. A recent computational study (R-CP + C_2H_4) suggests a strong *anti* preference for SiH_3, (260) the closest analog of the $(Me)_3Si$ group in the quinone adduct illustrated. These effects are subtle and not well understood, and it may be premature to attribute the rDA rate enhancement to metalloid properties of the $(Me)_3Si$ group.

3.3. Scavengers

Many rDA reactions have been carried out in the presence of an added diene or dienophile, different from the embedded educts. The intent is typically (a) to intercept a reactive educt (b) to prepare the new cycloadduct for use in synthesis or (c) to prevent back (DA) reaction by removal of one of the rDA products. Although the added reagent may properly be labeled a scavenger regardless of these distinctions, the focus of this discussion will be on the last application.

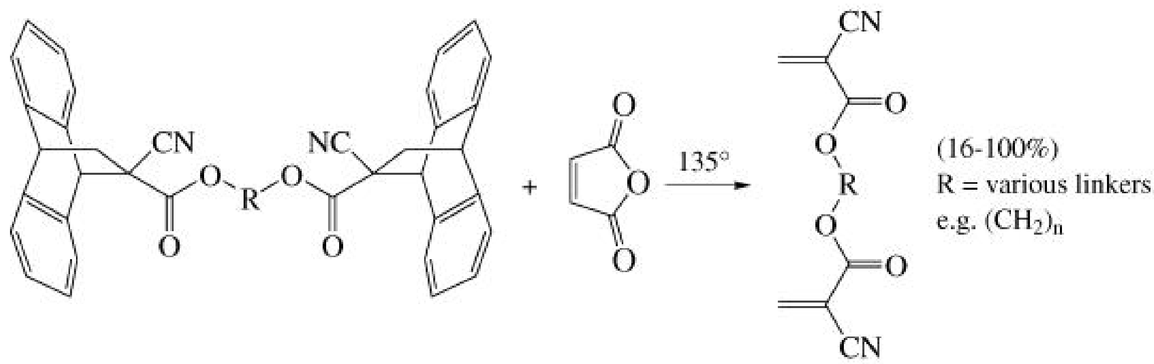
A classical paper by Diels in 1938 contains a number of innovations, including a description of the first rational synthesis based on the following scheme: 1) DA reaction; 2) functional group interconversion(s); 3) rDA reaction to form the desired product. The target, the diacid chloride of acetylenedicarboxylic acid, could not be prepared by the usual procedures available at that time. When the anthracene cycloadduct (after multistep preparation) was simply heated, none of the desired product was isolated. However, the addition of MA as scavenger to remove the anthracene led to formation of the acid chloride in unspecified yield. (261)



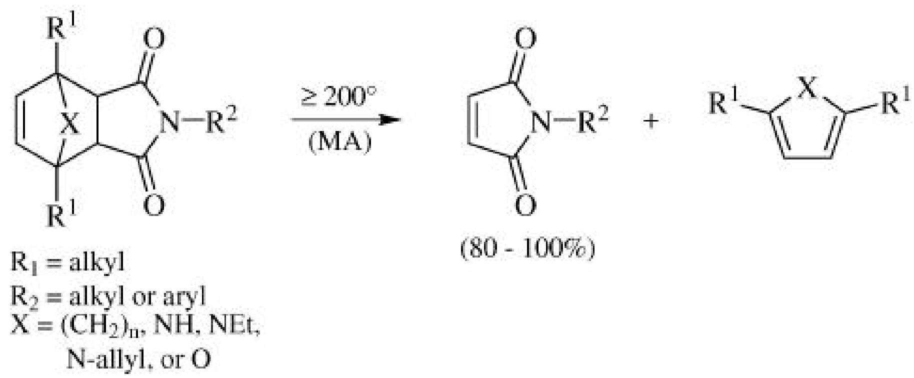
It should be noted that this conceptually novel experiment could not be reproduced when attempted several years later by duPont chemists. (262) In spite of this cloud, it is instructive to consider the rationale behind the use of MA in this experiment. The authors chose MA based on earlier observations that its cycloadducts appeared to be exceptionally stable, and it was also recognized that MA is relatively reactive compared to other common dienophiles. Together, high reactivity of educt and stability of cycloadduct define a good scavenger; the term "*avidity*" was suggested by Diels to describe this combination of kinetic and thermodynamic properties. (261)

Scavengers are often used in large excess, typically because the relative stabilities of the substrate and new adduct are not known. Additional thermodynamic information is needed in order to allow optimization of scavenger choice and to avoid the cost and waste inherent in use of excess material.

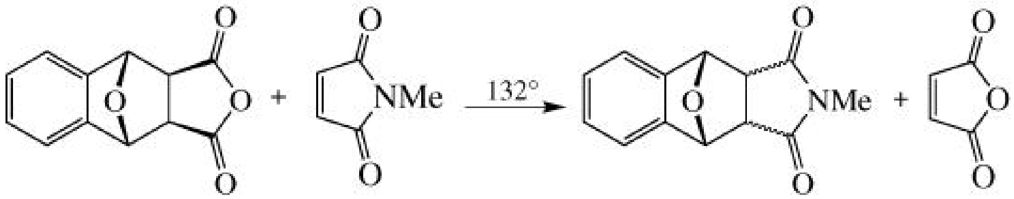
By far the largest percentage of scavenger applications involves added dienophiles; i.e., the purpose is to remove the diene from the equation and allow the isolation of the educt dienophile. MA continues to be the most widely used scavenger. It has proved especially useful in large-scale preparations of methylene-malonate diesters (263, 264) and highly reactive cyanoacrylates (265) from anthracene adducts.



Curiously, addition of MA (large excess) is also described in patents dealing with the preparation of maleimides by rDA reactions, although it is not clear that the use of MA resulted in any improvement in the already excellent yields obtained in the absence of scavenger. (266)



Recent work has shown that *N*-methylmaleimide (NMM)-furan and -isobenzofuran cycloadducts are 3 to 4 kcal/mol more stable than the MA analogs. (267) This difference allows determination of rates of otherwise kinetically inaccessible rDA reactions such as that of the *exo* MA adduct depicted.

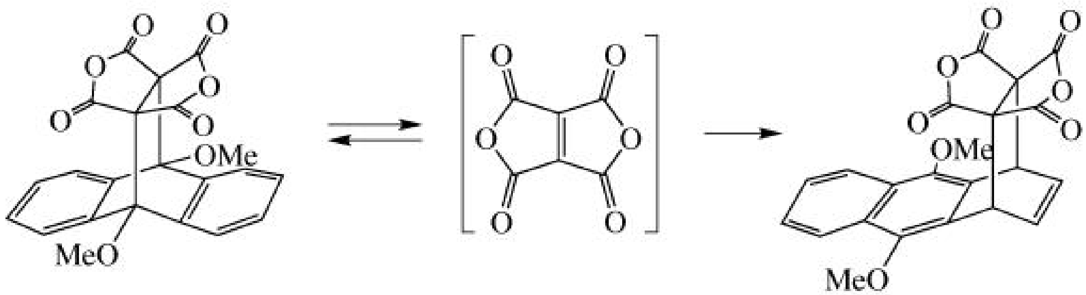


MA and NMM exhibit very similar reactivity in DA reactions with a wide range of dienes. However, NMM is clearly superior to MA as a scavenger, and other maleimides appear to share this characteristic.

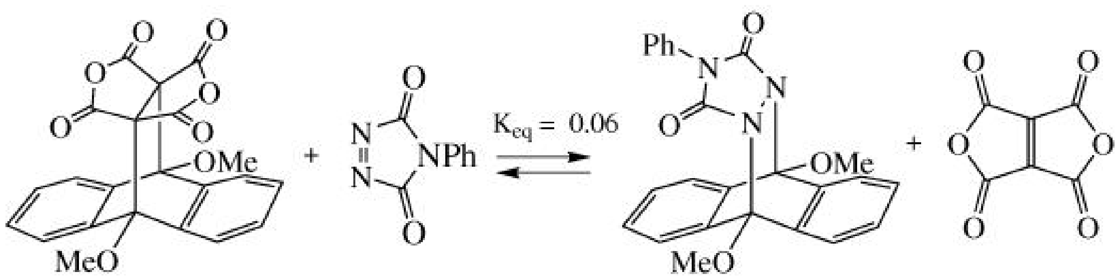
MA has been used to scavenge CP in rDA reactions used to prepare enones and similar embedded dienophiles, often under acid-catalyzed conditions. (208-210) MA has also been used to scavenge 5-trimethylsilyl-CP. (258) Although comparisons with MA were not made, NMM has proved useful in protic acid-catalyzed reactions that generate CP and (protonated) imines, (198) as well as for removal of *N*-methylisoindole generated in $LiClO_4$-catalyzed rDA reactions of various substrates. (220) Another occasionally used scavenger is acrylonitrile [for CP, (208) and $(Me)_5$-CP], (211) although there is no evidence that it is especially favorable for these purposes.

Although many different dienes have been used to trap reactive intermediate dienophiles, no systematic study of adduct stability has been reported. Excess 1,4-diphenylbutadiene has been employed, with limited success, as a scavenger of MA in preparations of substituted butadienes, cyclohexadienes, (268) and azulenes. (268a)

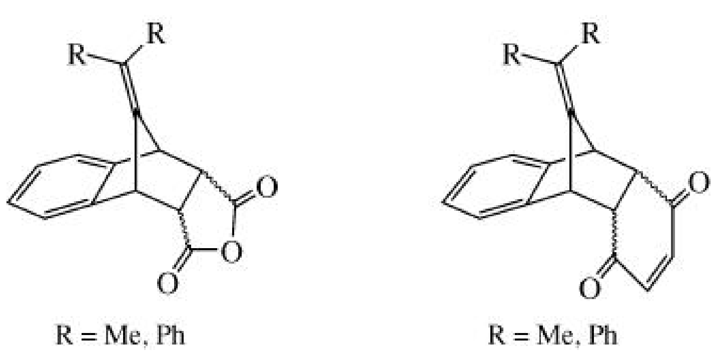
The very reactive dianhydride shown illustrates several features of scavenger use. This dianhydride is too reactive for simpler preparation or isolation, and closure of the second anhydride ring must be done after cycloadduct formation. The adduct with 9,10-dimethoxyanthracene dissociates readily (40°, dioxane); the dienophile has been trapped by CP, (269-271) dimethyl- and diphenylfulvene, (271) norbornadiene ([2 + 2 + 2] reaction), (270) 2,3-dimethylbutadiene, (271) chloroprene, (271) and 1,4-diphenylbutadiene, (271) but unfortunately the relative stabilities of the scavenger adducts have not been determined. Interestingly, in the absence of an added scavenger diene, the educts recombine by reaction at the terminal ring. (271)



N-Phenyltriazolinedione (PTAD) has been used occasionally as a scavenger of dienes, e.g., for pyrrole, (272) and more recently it has been directly compared with the dianhydride, with the latter exhibiting higher “avidity”. (273)



Unusual adduct thermal stability may signal the incorporation of a potentially good scavenger. For example, the dimethyl- and diphenylisobenzofulvene adducts proved to be very thermally stable, as evidenced by the lack of interconversion when the *endo* and *exo* isomers were separately heated to 180°. (274) This adduct stability presumably derives from the instability of isobenzofulvenes. It is unlikely, though, that isobenzofulvenes will find much use as scavengers, given the difficulties in their preparation.



An early mechanistic study of the *endo* to *exo* MA-CP adduct interconversion utilized the very reactive tetracyanoethylene (TCNE) as a scavenger for free CP, but mechanistic conclusions were obviated when it was realized that the TCNE adduct itself undergoes rDA reaction at the temperature employed. (135) There is no universal relationship between reactivity of educt and (in)stability of adduct, as shown also by the MA/NMM comparisons mentioned previously.

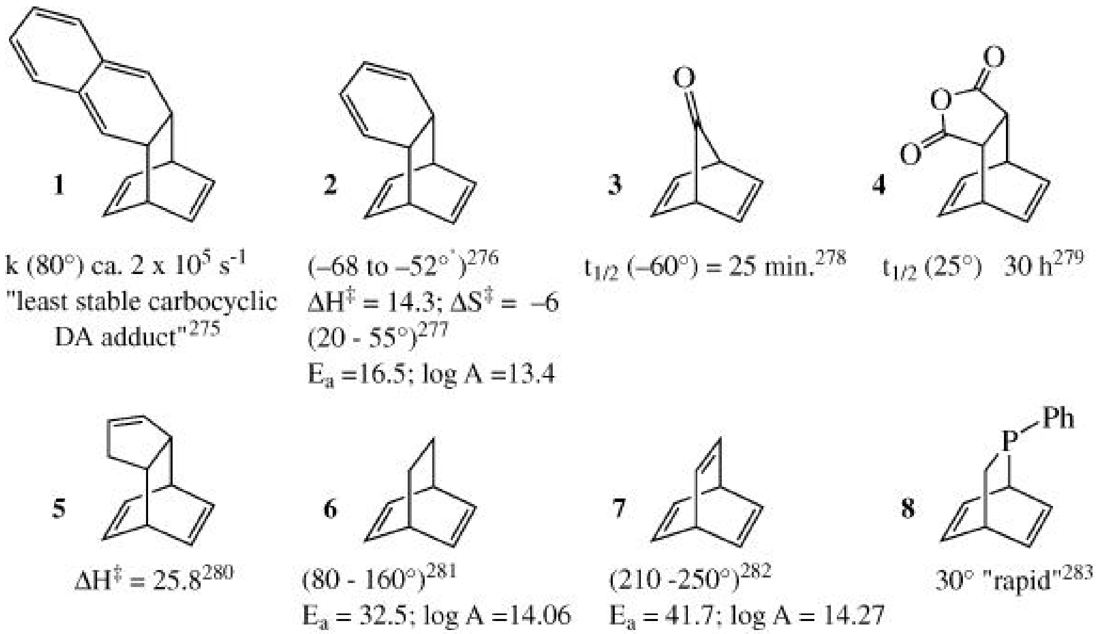
3.4. Reactivity Comparisons

Knowledge of the relative ease of expulsion of common dienes and dienophiles is of fundamental importance for synthetic applications of rDA reactions. Bearing in mind the usual caveat about the hazards of generalization, evidence outlined in this section suggests the following conclusions for the rDA reactivity of embedded educts as indicated:

Diene : furan,
pyrrole > benzene > naphthalene > fulvene > CP > anthracene > butadiene

Dienophile : N_2 > CO_2 > naphthalene > benzene, nitriles > MA > NMM, NPM > CP, imines, alkenes > alkynes.

Data in support of these relationships are often indirect, and not based upon absolute or relative rate determinations under identical conditions. Nonetheless, relative reactivity inferences can be drawn. To illustrate, adducts **1–8**, which decompose to benzene as a common "diene" fragment, are shown; the cheletropic loss of CO is included (**3**), to point up the facility of this reaction.



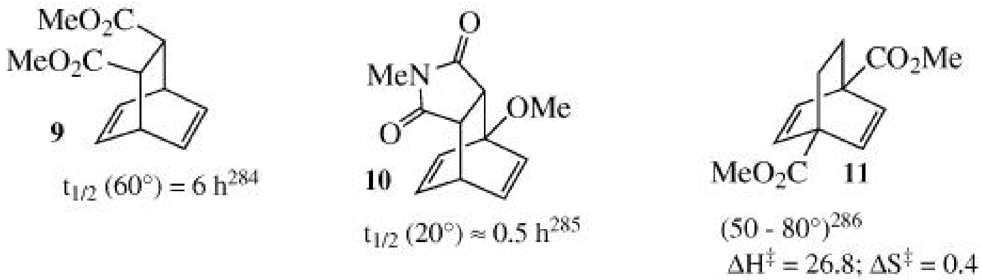
Naphthalene as the embedded dienophile (**1**) is expelled more readily than benzene (**2**), in keeping with expectations based on resonance stabilization effects in the developing products.

Comparison of **6** with barrelene (**7**) shows that ethylene is expelled much more readily than acetylene.

Expulsion of a conjugated diene (CP from **5**) is more facile than loss of a non-conjugated olefin, exemplified here by **6** but supported by other more closely related reactions.

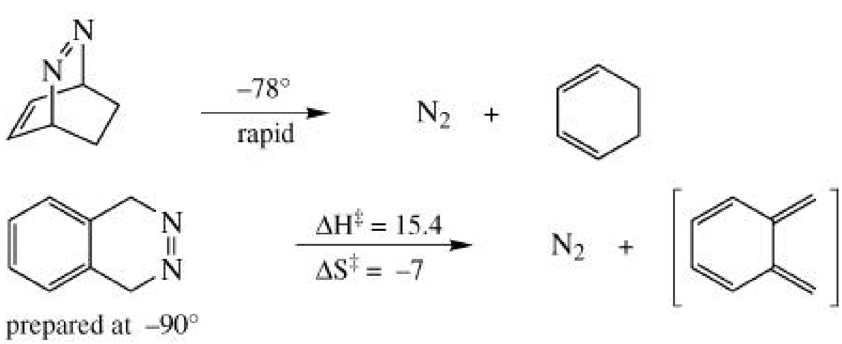
The MA derivative **4** is, perhaps surprisingly, relatively unreactive. The half-life corresponds to k(25°) »6.4 × 10^{-6} s^{-1}, similar to the rate constant for the *exo* MA-furan adduct, and substantially slower (ca. 10^3) than *endo* MA-furan adduct, (141) leading to the furan > benzene (as diene) relationship noted above.

Three related substrates are informative. The maleate derivative **9** is less reactive than the MA derivative **4**, paralleling the behavior of these dienophiles in typical DA reactions (MA > maleate). Although the NMM adduct of benzene itself has not been reported, we would expect it to be more stable, and less reactive, than **4**. The fact that **10** appears to be more reactive than **4** may be due to the effect of the bridgehead methoxy substituent. Interestingly, the bridgehead ester groups in **11** enhance reactivity relative to **6**, in contrast to the modest decrease observed for analogous substitution in the anthracene-methyl acrylate substrate, (175) previously discussed in the section on mechanism.



Clearly no single factor (e.g., resonance stabilization) rationalizes all these rDA rate relationships. It is worth noting that the far more extensively studied question of DA structure/reactivity has led to an empirical linear relationship that spans an impressive range of 10^{20} in rate. (44) The three factors that enter this equation are a) the HOMO/LUMO energy levels of educts, b) the distance between the reactive centers in the diene and in the dienophile, and c) the D H° for the overall reaction. No similar treatment of the rDA reaction has been reported, but the same factors would be expected to play a role (microscopic reversibility).

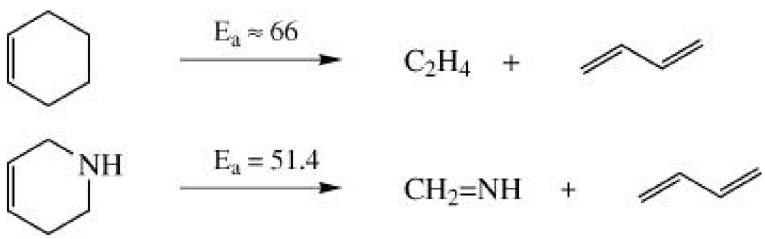
Unfortunately, simple heterodienophile cycloadducts of benzene (as diene) are mostly unknown, with **8** being the only representative of this important class with relative reactivity information. It would be of interest to add the dienophiles HCN, CH_2O , CO_2, O_2, and N_2 to this list. Clearly the expected high reactivity of at least some of these cycloadducts explains the absence of information. For example, the loss of N_2 to generate cyclohexadiene occurs rapidly at –78°, (287) and even *o*-xylylene is formed with the modest activation energy shown at temperatures above –90° in spite of disruption of benzene aromaticity. (288) One would expect the unknown adduct of benzene and N_2 to be extremely reactive, if capable of finite existence.



FVP temperatures needed for 50% conversions of two additional substrates that generate *o*-xylylene, through loss of CH_2O and CO_2 respectively, are shown. (289) These observations suggest that loss of CO_2 occurs more readily than loss of CH_2O . The rDA reactions that eject heterodienophiles are the subject of Part II of this review, to be published later.

FVP, 685° (50% conversion)   FVP, 570° (50% conversion)

The prototypical rDA reaction of cyclohexene to form C_2H_4 and butadiene has been extensively studied, and activation energies under different conditions have been determined. The more recent studies show that a temperature of ~500° is needed, with E_a » 66 (see Table II). The analogous gas phase formation of methyleneimine and butadiene occurs more readily. (290)

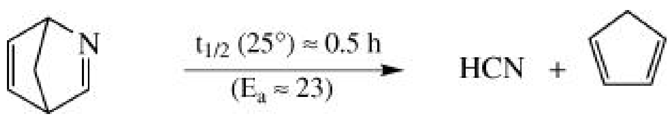


Norbornenes are generally good rDA substrates, forming olefins and CPs. In contrast, norbornadienes are rarely useful, although a few examples of expulsion of acetylenes from these adducts are known, and this course is favored when the “CP” that is expelled is a fulvene (see Table I). The alternative mode of decomposition commonly observed with norbornadienes is cheletropic expulsion of a carbene, with concurrent formation of benzene. The loss of CO from **3** is an extreme example. The favored pathway is strongly dependent on the substituents present at the “carbene” site. A review of this topic has appeared. (291)

Norbornene itself conveniently decomposes to C_2H_4 and CP at temperatures ³260°. (292)

Comparison with the cyclohexene system is informative. CP is ~10^3 times more reactive than butadiene in typical DA reactions. The fixed s-*cis* diene geometry and shorter C_1 - C_4 distance of the diene termini in CP are thought to be major contributing factors to the enhanced reactivity. It is noteworthy that a parallel large rate difference is found in the rDA reaction.

An approximate half life for the thermally unstable 2-azanorbornadiene has been reported. (293) This value corresponds (with the assumption that △ $S^{\ddagger}$ = 0) to E_a » 23.



The large rate enhancement caused by the heteroatom is especially evident in this instance, since the rDA reaction of norbornadiene (to acetylene + CP) has E_a » 50. (294)

Many other gaps in the rDA comparative reactivity literature will be clear to the interested reader.

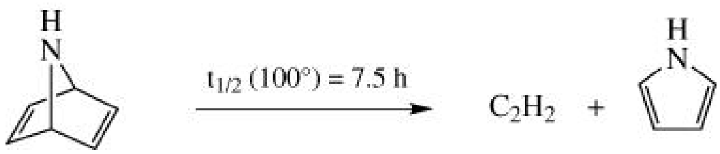
The organization of the remainder of this review is by type of expelled dienophile, in the order that these various dienophiles are tabulated (see Organization of Tables). Brief commentary is offered on each dienophile type.

3.5. Acetylenic Dienophiles

Reactions that generate acetylenic (including substituted) dienophiles comprise a relatively small class of rDA processes, and all entries are included in Table I.

As noted in the preceding section, substrates that expel acetylenes tend to be much less reactive than analogs that expel olefins. Thus, unlike cyclohexene, when 1,4-cyclohexadiene is heated, almost exclusive formation of hydrogen and benzene is observed, with only minor amounts of C_2H_2 plus butadiene. (295)

Although pyrroles enter into DA reactions reluctantly, several examples are known. Temperatures near 200° are needed, and typically the intermediate 7-azanorbornadienes decompose by rDA reaction under the reaction conditions, with formation of a (new) pyrrole and acetylene. The parent 7-azanorbornadiene has been prepared by alternative means; it gives facile rDA reaction at »100°. (296)

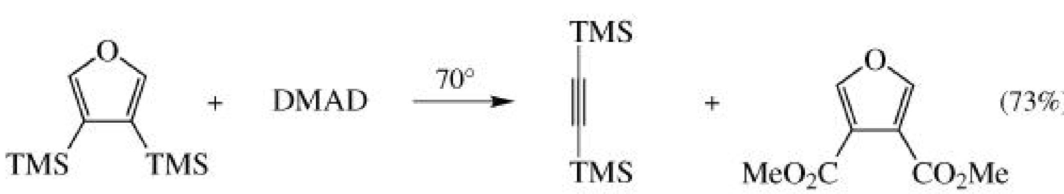


Reactions of pyrroles and similar dienes with substituted acetylenic dienophiles such as DMAD often give products that appear to involve the preferential loss of C_2H_2, but usually the reversibility of the DMAD reaction has not been examined, and the isolated product may simply reflect physical loss (e.g. evaporation) of a volatile product.

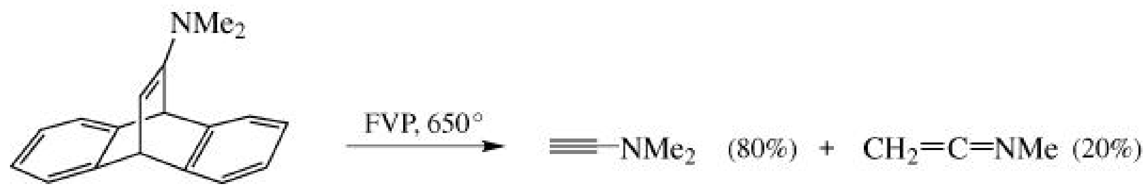
The parent 7-oxabicyclo[2.2.1]heptadiene is known to enjoy at least moderate thermal stability, although its rDA reactivity has not been quantitatively evaluated. The dibenzoyl derivative affords dibenzoylacetylene in high yield (furan not isolated) on moderate heating. (297)

Adducts of this dienophile and other dienes were also studied. The temperatures (100, 160, 210, and 260°) needed for rDA reaction suggest the order of reactivity: furan > CP > 1,3-diphenylisobenzofuran > anthracene. (297)

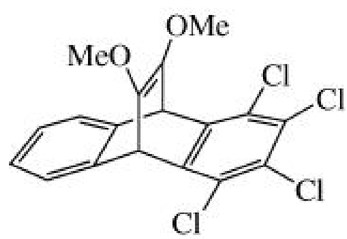
A 3,4-(bis)silylated furan reacts with DMAD in a DA-rDA sequence at mild temperature. Although bis(trimethylsilylacetylene) is difficult to isolate from this and related reactions, it appears to be easily generated in rDA reactions. (298)



Anthracene cycloadducts tend to be thermally robust, and generally can be expected to give clean rDA reactions without interfering side reactions. This generalization holds for acetylenes; simple alkyl and aryl substituted dibenzobarrelene derivatives yield alkynes in good yields when subjected to FVP at ³500°. (299) Among the more unusual applications, an enamine was used to generate the corresponding ynamine, with some demethylated byproduct. (300)



Among the few apparent failures of potential anthracene-forming rDA reactions, attempts (with $CP(Cl)_6$) to trap dimethoxyacetylene or demonstrate its formation by heating the tetrachloro adduct in solution (200°) or by FVP (450°) gave no sign of the alkyne. However, the expected tetrachloroanthracene was isolated in 50–75% yields. The authors suggested that decomposition gave two (MeOC) fragments. (301)



Although not conclusively demonstrated, formation of the "acetylenic" dienophile benzyne has been proposed for the decomposition of triptycene radical cation in the presence of $AlCl_3$, with anthracene radical cation coproduct. (302)

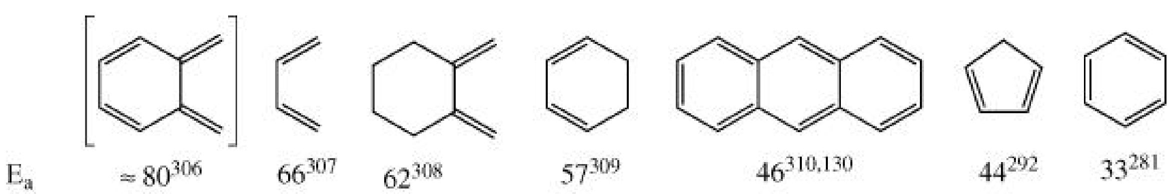
3.6. Ethylene

Table II is devoted exclusively to reactions that generate unsubstituted ethylene. Separation from other simple olefinic dienophiles is based primarily on the volume of literature, rather than fundamental differences in reactivity. Indeed, intramolecular and other comparisons indicate that a simple alkyl substituent on the embedded dienophile has very little effect on the rate of reaction.

As the parent carbocyclic rDA reaction, dissociation of cyclohexene has received a great deal of attention. Several methods of heating have been employed for thermal reactions, including flow pyrolysis, shock tube treatment, and pulsed IR lasers. The energy needed to effect an rDA reaction may also be introduced photochemically. The use of specifically deuterium-substituted cyclohexenes showed that, to a first approximation, the usual stereochemical outcome was observed with 185 nm UV as the energy source, whereas 105 nm light gave extensively scrambled products. (303) In thermal reactions, the normal stereochemical features are found even when carried out at temperatures ³800°. (304)

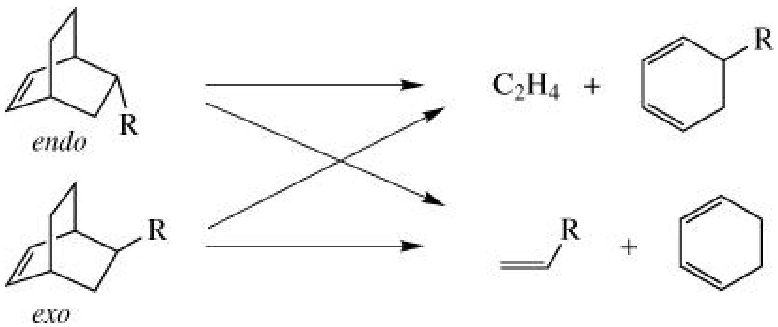
Numerous 1-, 2-, and 3-substituted cyclohexenes that expel ethylene upon heating are tabulated. Often rather high temperatures are employed, especially in FVP reactions. An unusual example is cyclohexanone, which presumably reacts via the enol to form ethylene and methyl vinyl ketone (via its enol). Various deuterated analogs were examined, giving products predicted by this mechanism. (305)

Activation energies for rDA reactions that share the common feature of ethylene formation are related to the stability of the diene fragment in more or less expected fashion. Several dienes that illustrate this feature are shown:



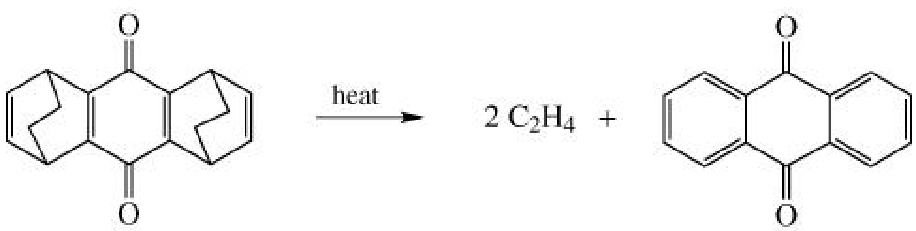
The reaction of tetralin to form ethylene and *o*-xylylene (first entry above) has been examined under a variety of conditions (see Table II), and the nuances of the reaction have been discussed. (311)

The reactions of *endo* and *exo* alkyl-substituted bicyclo[2.2.2]octenes have been carefully examined for R = Me, Et, and *i*-Pr. In general the effects of both substituent and stereochemistry are quite small, with E_a values for essentially all of the 12 pathways falling in the range 58.5 ± 1.0 (see Table II for specifics). (312)



A similar study for R = CN showed the expected preference for expulsion of acrylonitrile relative to ethylene, again with little, if any, stereochemical dependence. (313)

rDA reactions that expel ethylene with concurrent formation of an aromatic ring are important both historically and in modern synthesis applications. The earliest examples (1929) arose in observations by Diels, Alder, and their coworkers that adducts of quinones and 1,3-cyclohexadienes, after oxidation to generate bicyclo[2.2.2]octadiene substructures, gave ethylene and the homologated quinone. Even bis rDA reactions were reported at this early stage. (314)

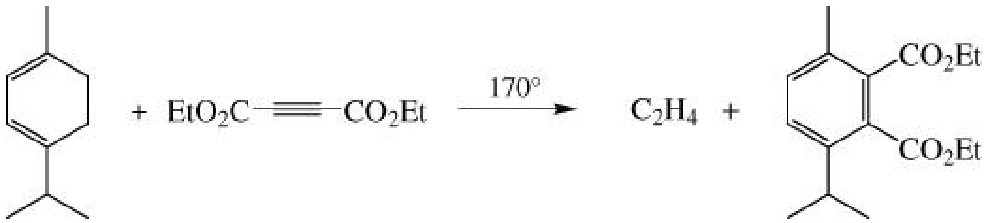


The fundamental reaction described in this early work has been used many times for the synthesis of substituted naphthoquinones, anthraquinones, tetracenequinones, and heterocyclic analogs, as shown by the numerous entries in Table II.

The “Alder–Rickert” reaction was introduced as a method of distinguishing 1,3-cyclohexadienes from other dienes that also gave DA adducts, e.g., CP and cyclo heptadiene.

The formation of ethylene (plus phthalate ester) when the diene was heated with DMAD or its ethyl ester analog, signaled the presence of a

1,3-cyclohexadiene. The reaction has been used to help determine the structures of some terpenes, such as α -phellandrene (132) and α -terpinene. (315, 316)



The failure to produce ethylene or other volatile olefins under Alder–Rickert conditions has been used to help locate DA-active diene sites, as nicely demonstrated in early work on levopimaric acid. (317) The reaction with DMAD (150°) followed by GLC analysis of gaseous products has also been employed for determination of the composition of mixed substituted cyclohexadienes. (318)

Many substituted acetylenes have been employed in the syntheses of aromatics, following the Alder–Rickert principle. These are listed according to increasing acetylenic substituent oxidation state in Table II. Quinones have also been employed in analogous manner, relying on the facile air oxidation of cycloadduct intermediates which allows quinones to serve as “acetylene equivalents” in one-pot DA-oxidation-rDA sequences.

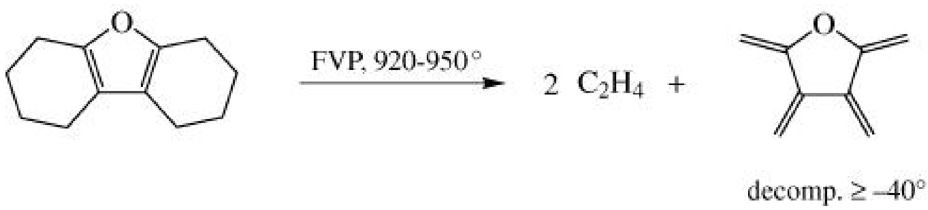
Only 1,3-cyclohexadienes give Alder–Rickert reactions, but methoxy-substituted 1,4-cyclohexadienes can serve as substrates under conditions where equilibration of dienes occurs. This important observation opened the door to the direct use of Birch reduction products of anisoles, and several synthetic applications have appeared. Curiously, the use of dichloromaleic anhydride as a catalyst for this purpose has assumed almost folkloric proportions, even though the original users stated that it was not unique for this purpose. (319) It is likely that diene interconversion is acid catalyzed, and indeed trifluoroacetic acid works well for the Alder–Rickert reaction of 1-methoxy-1,4-cyclohexadiene itself with DMAD. (320)

Dichloromaleic anhydride catalyst does not lead to successful Alder–Rickert reaction for the Birch reduction products of toluene or xylene, (321) stressing the importance of the methoxy group for this use of 1,4-dienes.

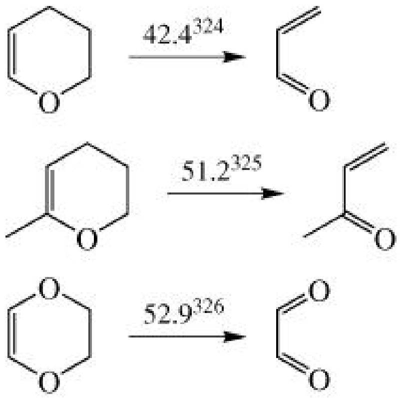
Several heterocycles are readily accessed through rDA reactions with expulsion of ethylene; these include pyrroles, and many substituted furans have been prepared using this step. Kinetically metastable products such as isoindoles and isobenzofurans have also been formed in this manner, usually in highly efficient reactions. The parent isobenzofuran has been made in quantitative yield as shown. (322)

Several more complex analogs, including bis and tris(furans), have been formed in related reactions, as shown in the table.

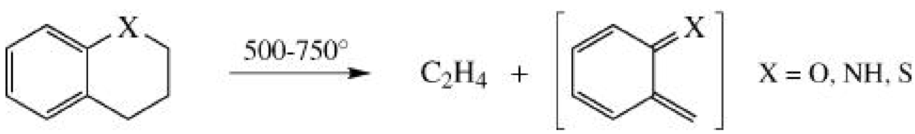
The very reactive tetramethylenetetrahydrofuran is formed under FVP conditions by the expulsion of two equivalents of ethylene from the substituted furan depicted: (323)



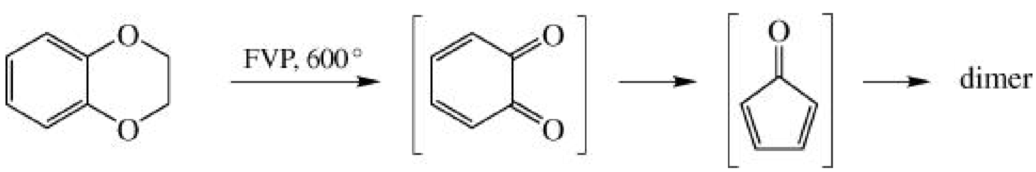
Six-membered heterocyclic 2-enes evolve ethylene with the formation of carbonyl compounds or azo or thio analogs. Three oxacyclic examples for which E_a values have been reported are shown. The E_a value for dihydropyran itself appears to be unexpectedly low in this comparison, but it is clear that all three substrates undergo rDA reaction much more readily than cyclohexene (E_a = 66).



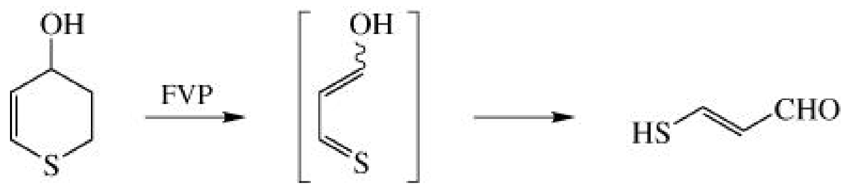
Heterocyclic analogs of tetralin behave in the expected manner to form *o*-quinomethanes and azo and thio analogs. (327)



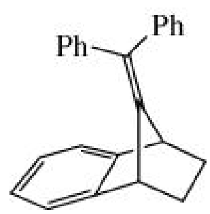
These reactions have also been explored at 1000° under FVP conditions. (328) The dioxa derivative, when subjected to FVP at 600°, presumably generates *o*-quinone as a fleeting intermediate that loses CO to form cyclopentadienone, which is isolated as the DA dimer. (329)



One of the important uses of rDA reactions involves the formation of enols and similar metastable materials. An interesting example is shown, in which the enol that is presumably generated is also a thioaldehyde, itself a metastable functional group that usually cyclotrimerizes. In this instance proton migration leads to the more stable enethiol aldehyde. (330, 331)

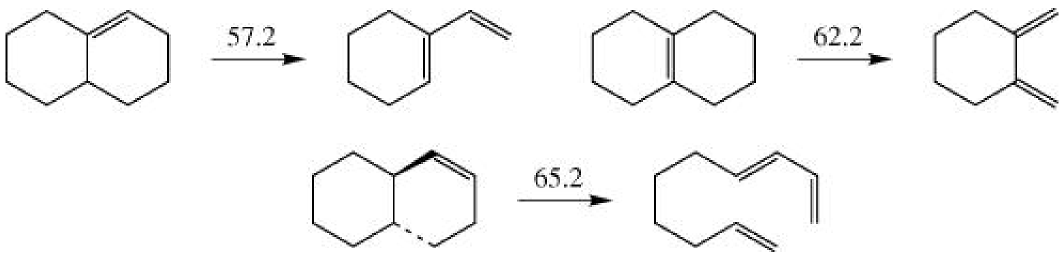


With only one known exception, substrates that can undergo rDA reaction with expulsion of ethylene will do so (unless a more facile decomposition pathway is available). The exception is the isobenzofulvene derivative depicted. No evidence of ethylene formation was found when this substrate was heated to 650°; instead rearrangement to indene derivatives and subsequent r[10 + 2] reaction was observed. (332) As noted earlier, lack of rDA reaction is typical of isobenzofulvene derivatives, regardless of the embedded dienophile.

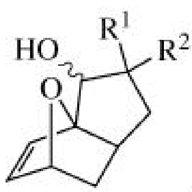


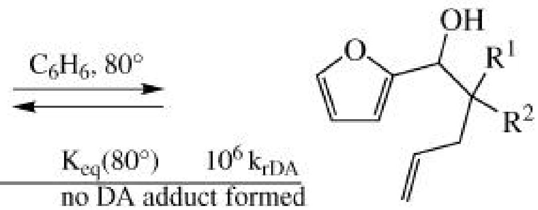
3.7. Monoalkyl Ethylenes

A single alkyl substituent on the embedded dienophile, even if relatively bulky, will have little effect on the rate of an rDA reaction (see discussion of substituent effects in the Mechanism section). The major new factor that enters the picture with the introduction of one (or more) substituents is the possibility of intramolecular reaction. While intramolecularity is commonly assumed (and in several instances known) to enhance the rates of DA reactions, the effect to be expected on the reverse process is less obvious. There is no definitive experimental answer to this question, since any change made in a substrate to force intramolecularity invariably will change other features of the reaction. To illustrate, three isomeric substrates and their rDA E_a values are shown. (308) The two intermolecular variants both expel ethylene; these differ by a few kcal/mol in a manner consistent with diene stability arguments (endocyclic double bond favored over exocyclic). The intramolecular reaction has the highest E_a of the three, but the increase may be due to lower ring strain in the starting material rather than any intrinsic cost of intramolecularity. Further context is provided by the rDA reaction of 4-methylcyclohexene to form propene and butadiene, which has E_a = 66.6, (333) essentially identical to the E_a for cyclohexene dissociation, and most similar to the intramolecular reaction illustrated, suggesting that the latter is the “normal” value.



Furan derivatives are useful substrates for the study of substituent effects on intramolecular DA/rDA reactions, owing to relatively high reactivity. Some effects of *gem* substitution are shown. (334)

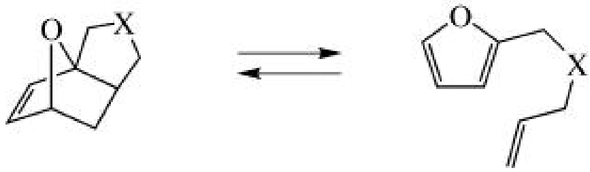




R^1	R^2	$K_{eq}(80°)$	$10^6\,k_{rDA}$
H	H	no DA adduct formed	
Me	Me	>20	—
$(CH_2)_5$		1.1	1.62
n-Pr	*n*-Pr	0.71	1.95
$S(CH_2)_3S$		0.31	1.86
SEt	SEt	0.18	1.22
OEt	OEt	0.21	3.04

These reactions were actually studied experimentally in the DA direction, and the K_{eq} and rate constants have been recalculated to provide the rDA perspective. Except for R = H or Me, for which rate constants were not determined, the other substituents lead to relatively small kinetic effects, somewhat greater on the DA than on the rDA direction. The fact that the cycloadducts may exist as (undetermined) mixtures of diastereomers unfortunately clouds both analysis and conclusions about the *gem* substituent effects.

Heteroatom-containing 2-(4-alkenyl)furans provide a somewhat puzzling range of behavior. The tethered reactants (the rDA product) reportedly failed (up to 75°) to give cycloadducts with X = NH, O, or S, although for X = NH_2^+, a substantial amount of cycloadduct was isolated. (335) This (protonated) cycloadduct did not give rDA product on simple treatment with sodium bicarbonate solution, suggesting that the failure to obtain cycloadduct from the neutral X = NH species was not caused by a facile and unfavorable equilibrium.



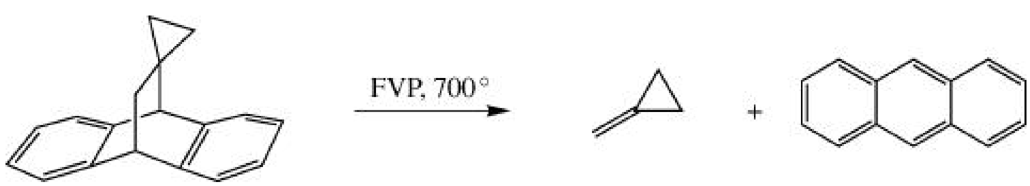
An earlier study of this system with X = NAr found that dissociation occurred on attempted vacuum distillation, while the DA cyclization took place upon standing at room temperature for a few days. (336)

The usual range of common rDA reactions, including several Alder–Rickert applications, and some homo-rDA examples that form monoalkyl ethylenes, are collected in Table III.

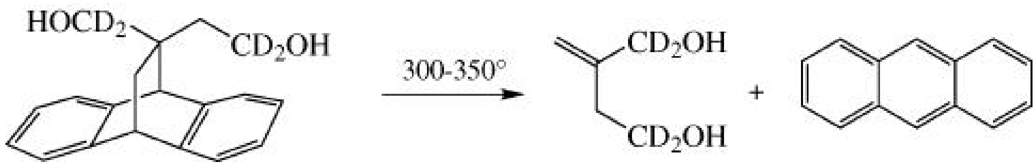
3.8. 1,1-Dialkyl Ethylenes

Although few in number, rDA reactions that form 1,1-dialkyl ethylenes have been separately tabulated for ease of reference (Table IV), and to segregate them from the far more numerous 1,2-dialkyl ethylene-forming reactions that are displayed in Table V.

Most rDA reactions that generate 1,1-dialkyl ethylenes involve bicyclic substrates ([2.2.1] and [2.2.2], Alder–Rickert reactions that generate the latter, and anthracene adducts). These reactions exhibit few unusual features, and require little discussion. An exception is shown in which methylenecyclopropane is formed in quantitative yield. (337) The high temperature appears to be critical, since it had previously been reported that this substrate exhibited unusual thermal stability, being unaffected by temperatures up to 450°. (338)



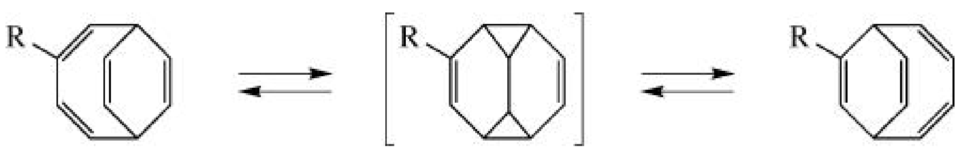
Several instances of the use of anthracene as an olefin protecting group have appeared in the literature. In one common application, cycloadduct formation prevents otherwise facile Michael addition or polymerization of the dienophile, as often observed when nucleophilic reagents are used with, e.g., unsaturated esters. These problems are circumvented for $LiAlD_4$ reduction by the sequence DA, reduction, rDA. The last step for one example is illustrated. (339)



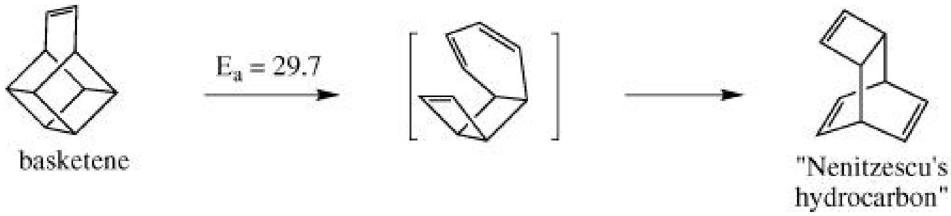
3.9. 1,2-Dialkyl Ethylenes

Unusual structures, and intramolecular rearrangements that include formal rDA steps, are encountered in this major category.

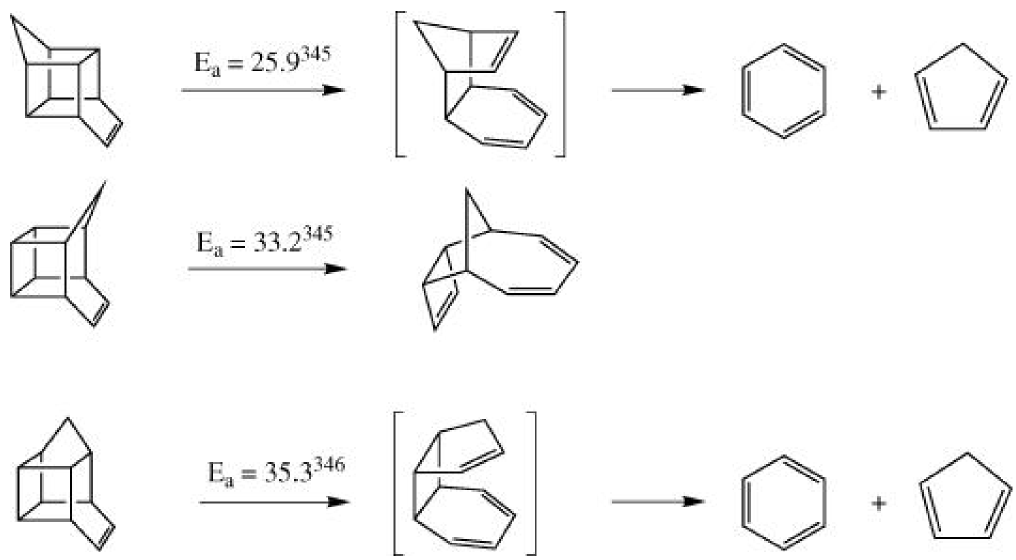
A facile intramolecular DA/rDA sequence accounts for the interconversion of [4.2.2]tetraene isomers. The diene intermediate for the degenerate reaction (R = H) has been independently synthesized, and found to give rapid rDA reaction even at –15°. (340) Substitution introduces asymmetry, which can result in appreciable preference for one tetraene isomer; for example, when R = Me, K_{eq} ³ 19. (341) Other examples can be found in Table V.



The rearrangement of “basketene” to “Nenitzescu's hydrocarbon” is believed to occur by rDA reaction to give the intermediate shown, followed by a 1,3 (allylic) shift. (342) At somewhat lower temperature the intermediate can in fact be isolated, (343) and an independent synthesis established that it is reasonably stable at 0°. (344)



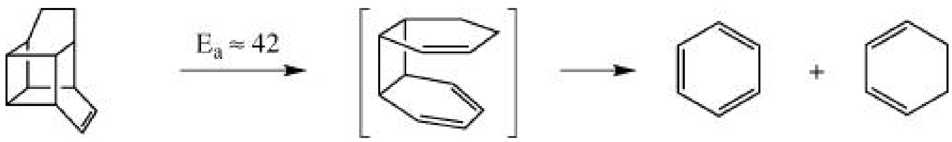
Three isomeric methylene homologs of basketene have been subjected to thermal decomposition. Formally, the first step for each is an rDA reaction that generates a cyclohexadiene and an olefin. The overall reactions, structures of possible or likely intermediates, and E_a values are shown. The most reactive and the least reactive substrates both give benzene and CP as final products, but with activation energies that differ by almost 10 kcal/mol.



As noted in an earlier section, the presumed intermediate in the upper (fastest) reaction has been independently synthesized, and its rDA reaction to form benzene and CP was found to occur with an E_a » 28. (174) Since this value is higher than the E_a for the overall process shown, the possibility arises that the intermediate might be isolable (entropy effects might alter this prospect). Conversely, the lower E_a for the overall reaction may signal direct formation of the products, without passing through the intermediate in its ground state. The intermediate rate reaction is more directly analogous to the rDA of basketene, and the difference in E_a values, now clearly both for rDA reactions, may be ascribed to the added methylene; among other factors, the diene C_1 - C_4 distance is presumably different.

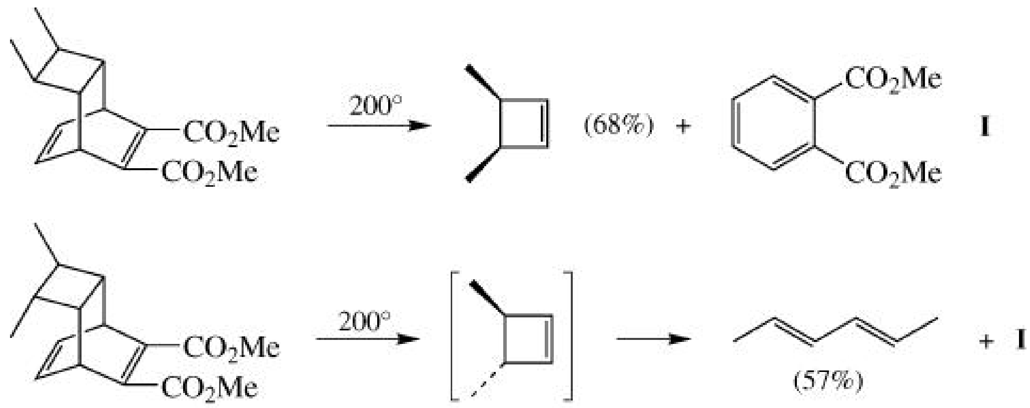
The slowest of these reactions differs from the fastest in two ways, again assuming that both occur via the intermediates shown, or transition states with related properties. The slow reaction lacks a plane of symmetry, and it can form the ultimate products only by r[2 + 2] reaction or allylic rearrangement followed by a second rDA step. It is not known that an intermediate is formed, or whether the higher E_a reflects a higher initial rDA barrier or difficulty with a second step.

The next higher homolog of this system has also been examined and exhibits an even higher E_a for a process that results in benzene and 1,3-cyclohexadiene as final products. (347)

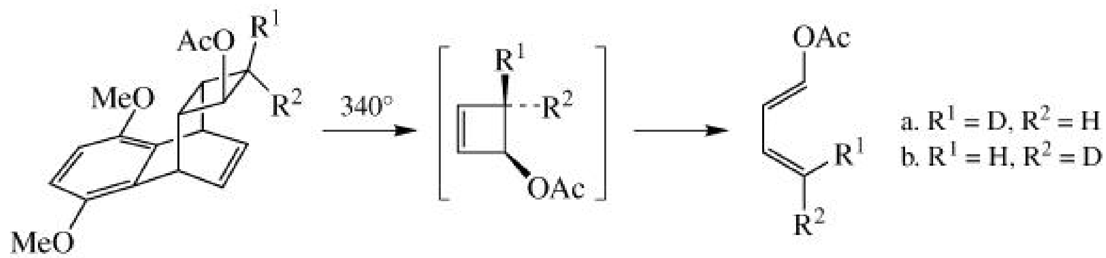


Small-ring olefins were early targets of syntheses via rDA reactions. Cyclopropenes, although likely (initial) coproducts in many reactions listed in Table V, have not been rigorously identified. Cycloheptatriene-norbornadiene interconverting systems were extensively studied by application of Alder–Rickert reactions, with the analytical focus usually limited to the aromatic “diene” product.

Early controversy developed with competing claims of formation of cyclobutenes vs. butadienes by rDA reactions. It is possible that both views are correct, since it is very difficult to reproduce experimental conditions exactly for high temperature flow reactions. Only recently have some of the nuances of substituent effects on the conrotatory cyclobutene-butadiene rearrangement become better understood. The effects can be quite striking; for example, a 3-ethoxy group lowers the activation energy for this (completely stereospecific) rearrangement by 9 kcal/mol. (348) Whether the initially generated cyclobutene from an rDA reaction can be isolated before rearrangement thus depends on experimental conditions and substituent effects. This point is nicely illustrated by the *cis* and *trans* 3,4-dimethylcyclobutene adducts. When carried out under identical conditions, the *cis* isomer affords the cyclobutene as the major product, whereas the *trans* isomer gives (*E,E*)-2,4-hexadiene. (349) The E_a for rearrangement of *trans*-3,4-dimethylcyclobutene is estimated to be »3.5 kcal/mol lower than the E_a for the *cis* isomer. (348)

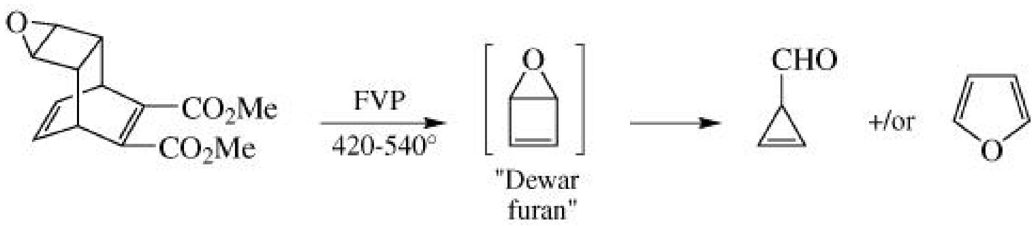


Groups such as methoxy, ethoxy, acetoxy, and chloro all tend to facilitate cyclobutene-butadiene rearrangement if the *E* product geometry demands of these electron-releasing groups can be met. This feature has been used in some rDA syntheses of specifically substituted butadienes, illustrated by the elegant work depicted. (350)



The substrates for many cyclobutene-forming reactions are formal cycloadducts of aromatics. Although this feature has the advantage of lowering the temperature needed to generate the strained olefin, the major reason is ready accessibility through DA reactions of cyclooctatetraene and acetylenic dienophiles (or equivalents such as quinones).

Fusion of a cyclobutene *cis* to another ring can prevent rearrangement to the butadiene isomer when conrotatory motion would lead to a highly strained small ring *E* cycloalkene. An effort to make the elusive “Dewar furan” that incorporates this feature is noteworthy, even though the presumed initial product was too unstable for isolation. (351)

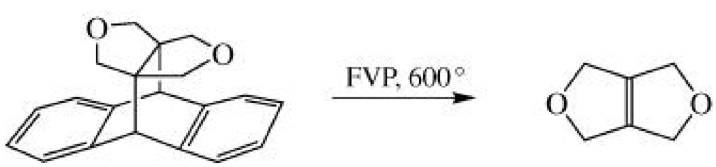


Many other 1,2-dialkyl ethylenes have been generated by rDA reactions, and these are included in Table V. Much recent work focuses on reactions that generate substituted furans as the diene component, making use of the relative ease with which this heterocycle is generated in thermal processes.

3.10. Tri- and Tetraalkyl Ethylenes

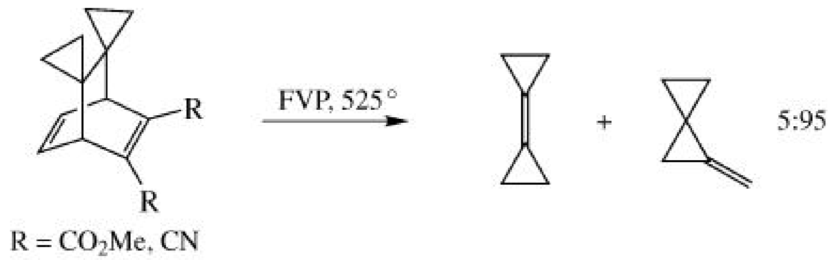
Although there are relatively few examples of rDA reactions being used to generate highly alkylated ethylenes, some novel chemistry is encountered in this class. Simple substrates appear to behave normally. For example, the tetraol shown is formed in good yield when the anthracene cycloadduct is heated at a “normal” 300°. (352)

The related diether is similarly isolated in quantitative yield by FVP. (352, 353)

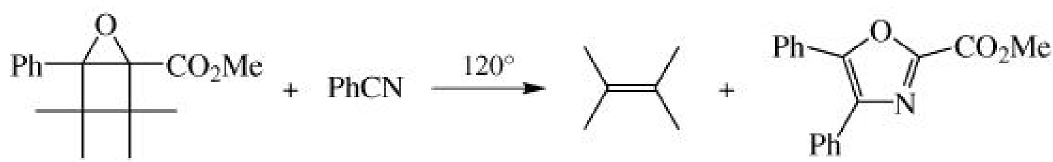


Thia ether analogs are similarly prepared by FVP at 700°. (354)

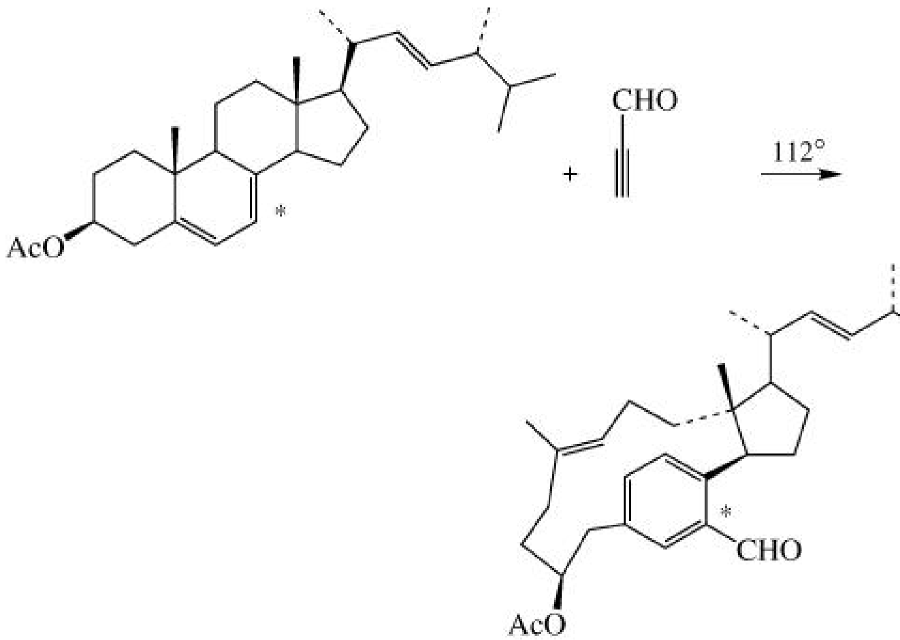
An rDA reaction designed to give cyclopropylidenecyclopropane gave instead a good yield of largely rearranged product. (355)



An unusual variant of the Alder–Rickert reaction is observed when a highly substituted cyclobutene epoxide is heated with DMAD. (356) It is thought that the addition occurs via the ring-opened dipole, since nitriles are trapped in similar fashion to form oxazoles. (356, 357)



Alder–Rickert type reactions have also been used with some steroidal dienes to generate rather complex and optically active paracyclophanes. (358-360) The intermediate cycloadduct has been isolated in some instances by carrying out the DA step at lower temperatures, with Lewis acid catalysts.



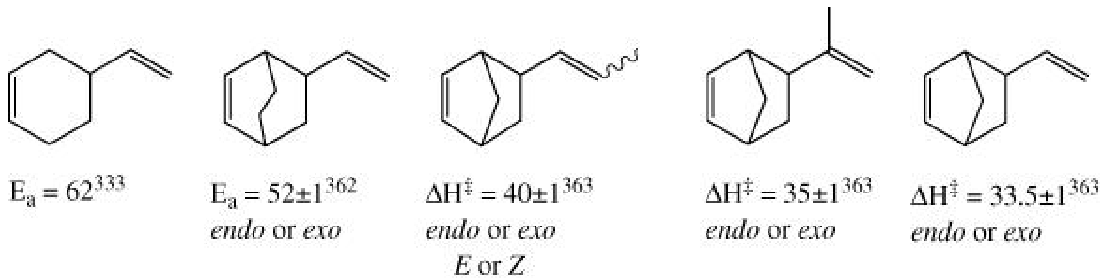
(85%)

3.11. Aryl- & Vinyl-Substituted Olefins

The introduction of a vinyl or aryl substituent on the embedded dienophile appears to lower the barrier to rDA reaction, in a system-dependent manner. It has been argued that the diminished barrier corresponds to the formation of a diradical intermediate (two-step reaction). (361) Experimental activation parameters for the "parent" 4-vinylcyclohexene reaction vary over a wide range (see Table VII); for comparison purposes we prefer the value $E_a = 62$, (333) reported from the same laboratory as the value $E_a = 66$ for 4-methylcyclohexene (this in turn is essentially identical to cyclohexene rDA, as noted previously).

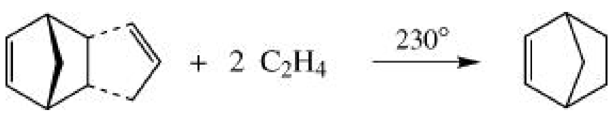
Only a single kinetic study affords a quantitative comparison of the effect of a phenyl substituent. (175) (See table in the Mechanism Section.) The expulsion of styrene occurs ~10^2 times faster than unsubstituted (or methylated) ethylene from the anthracene cycloadduct (250°), corresponding to an activation energy difference of ~5 kcal/mol.

Other studies support the general conclusion that double bond conjugation enhances the rDA reaction. Some structures and activation energies (or enthalpies) are listed below. To the extent that comparisons are possible, these substrates all react faster than their more saturated counterparts.

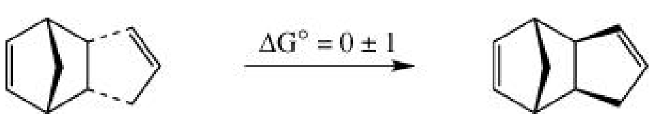


It is worth noting that neither the stereochemistry (*endo, exo*) nor *E,Z* structural difference has much effect on the rates of these rDA reactions, in contrast to the CP dimer system discussed below. However, an added methyl group has an appreciable effect, as shown by the last three entries. The barrier increase is greater on the terminal than on the internal site. The causes of this behavior are not obvious.

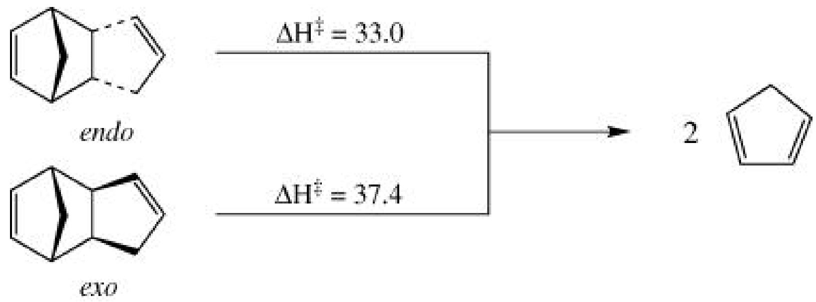
The dissociation of dicyclopentadiene, the DA dimer of CP, is one of the most important individual reactions in organic chemistry, because of the many uses of CP in both cycloaddition and organometallic applications (usually as the anion Cp). For most uses, the dimer is "cracked" and the CP is isolated and used within a relatively short time. Less commonly, an added in situ dienophile is used to form a new cycloadduct directly as the CP is formed. An example is the high yield reaction with ethylene to form norbornene. (364)



When CP undergoes DA dimerization, the strongly favored isomer is *endo* (kinetic control). The *endo/exo* equilibrium position is not accurately known, but it has been estimated that neither dimer is appreciably favored. (365)



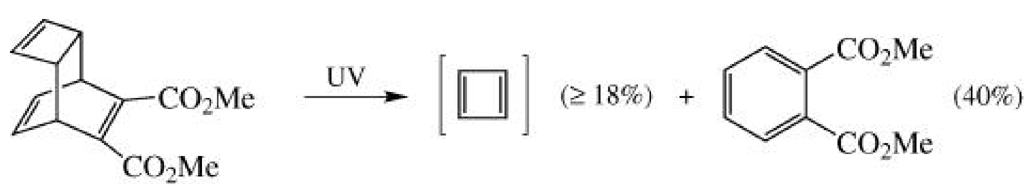
As required by these two facts, but in contrast to the similar materials discussed above, there is a sizable difference in the activation energy for dissociation of the *endo* and *exo* isomers of $(CP)_2$. (365, 366)



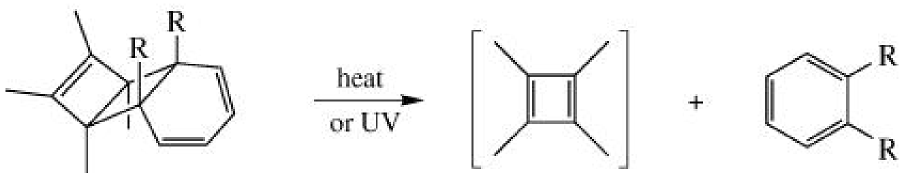
The conversion of *endo*-dicyclopentadiene to the *exo* isomer by thermal means is not a viable process. (366) At the temperature needed to crack the *endo* isomer, considerable CP is formed, and this leads to the formation of trimers and higher oligomers. Enriched *exo*-dicyclopentadiene can, however, be further purified if the CP formed by thermal decomposition of residual *endo* dimer is removed in vacuo while heating to 180°. (367) *exo*-Dicyclopentadiene is prepared by addition of HBr or HI to *endo*-$(CP)_2$ followed by base-induced elimination of HX. The addition occurs with Wagner-Meerwein rearrangement to form the *exo* bicyclic skeleton. (367-370)

The reason for the ~4 kcal/mol higher activation energy for rDA reaction of the *exo* isomer remains somewhat puzzling, especially in the context of other *endo, exo* isomeric pairs, which usually differ very little in activation energy.

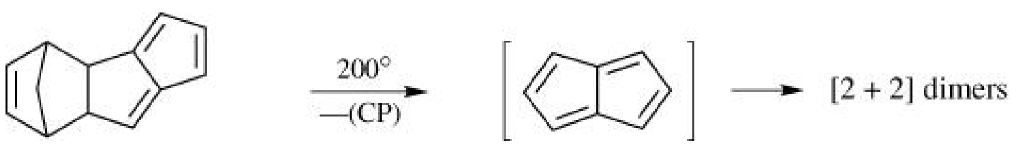
Cyclobutadiene was an early (1948) target of rDA methodology. The readily available cycloadduct of DMAD + cyclooctatetraene on heating gave a “tar” plus the expected dimethyl phthalate, probably signaling formation of this once-elusive species. (371) Stronger evidence for generation of cyclobutadiene by rDA reaction came nearly thirty years later, when UV treatment of the same substrate afforded ³18% of a trapped adduct of this reactive diene. (372)



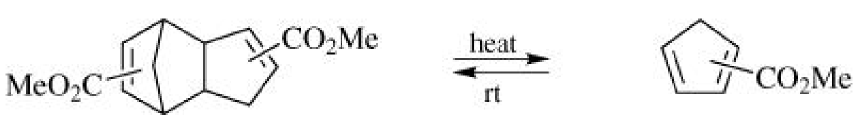
Similarly, evidence indicating formation of tetramethylcyclobutadiene was obtained either by heating or UV exposure of the diester (R = CO_2Me) or analogs. (373) Note that because of the unique symmetry of cyclobutadiene this dissociative process may be considered either a r[2 + 2] or r[4 + 2] reaction, the latter by viewing cyclobutadiene as the "diene" educt.



Pentalene is another of the very reactive species that have attracted rDA attention. Earlier studies had shown that a monomethylated derivative could be prepared by FVP. This methylpentalene could be isolated at –196°, but readily dimerized by [2 + 2] reaction at temperatures higher than –140°. (374, 375) Pentalene itself was generated as a fleeting intermediate by the reaction illustrated. (376)



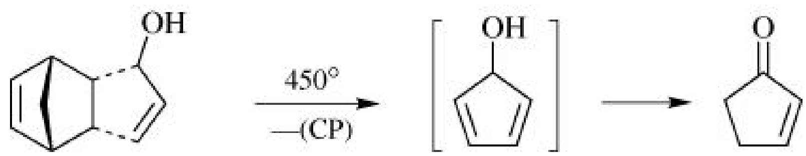
Substituted CPs, both as monomers and dimers, consist of a fascinating class of materials with a venerable history. It appears that Thiele's 1901 study includes the first example of what is now recognized to be an rDA reaction. [This work is sometimes cited as the earliest example of a DA reaction, but this honor (1887) belongs to Japp and Burton. (10)] Thiele prepared the pyrophoric solid potassium salt of CP, KCp, treated it with CO_2, and isolated the dimeric diacid ("Thiele's acid"). After esterification, attempted distillation of the presumed dimer gave monomeric ester, which dimerized again upon standing. (377)



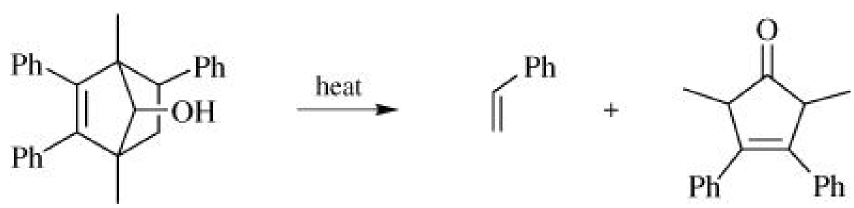
Over half a century later it was recognized that both the dimer and the monomer are thermally equilibrated mixtures of isomers, and later studies have been carried out in efforts to ascertain structures and activation parameters in this and related systems. (378, 379)

Several novel examples of substituted CPs formed by rDA reactions are shown in Table VII, including intramolecular and mechanistically informative processes. The chemistry is complicated by the possibilities of Cope rearrangement of the dimer, and 1,5-shift isomerization of the monomer. Several examples are included in the table, and a few are amplified here (see also Base-Induced Reactions).

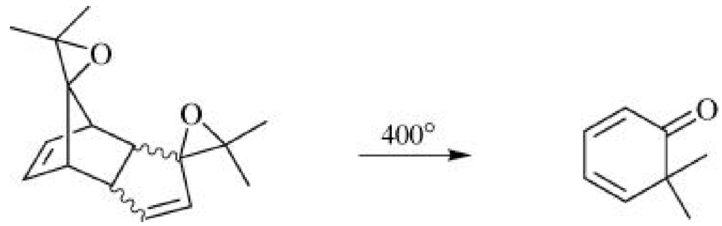
The instability of 2,4-cyclopentadienol is illustrated by an attempted rational synthesis using an rDA step. The actual product isolated was 2-cyclopentenone, probably formed by initial generation of the alcohol followed by a 1,5-shift and then enol-keto tautomerism. (380)



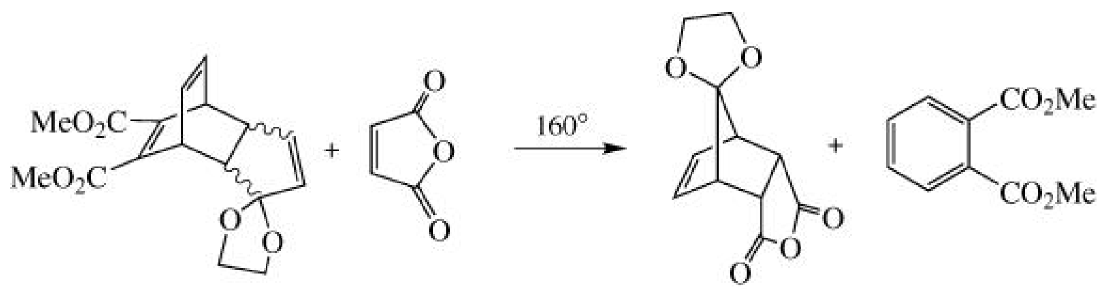
A similar sequence can account for formation of a substituted 3-cyclopentenone; loss of carbonyl conjugation is compensated by phenyl conjugation in this instance. (381)



Although the timing of the individual steps has not been demonstrated, and the stereochemical features remain undefined, the bis-epoxide dimer undergoes rDA reaction and ring expansion under pyrolysis. (237)

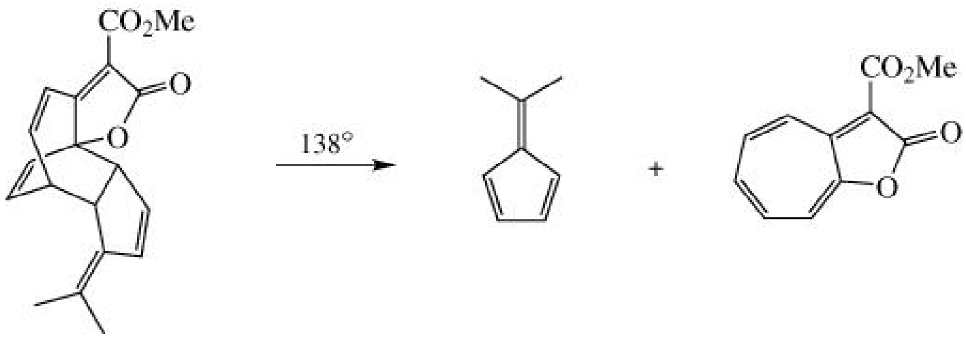


The many rDA and related reactions that generate cyclopentadienones (as dienophile educts) are discussed in the section dealing with mono-EWG alkenes. However, it is appropriate to comment here on the related ketals. The ethylene glycol ketal is especially interesting, giving DA dimer with k » 10^3 $M^{-1}s^{-1}$(25°), more than 10^5 faster than the dimerization of CP itself. (382) The rate is nonetheless much lower than the rate of dimerization of cyclopentadienone, which is believed to occur with k » 10^8 M^{-1} s^{-1}, near the diffusion-controlled limit. (383) Although dimerization of the glycol ketal is very fast, it is nonetheless possible to trap the monomer with a sufficiently reactive in situ dienophile such as MA. (384)

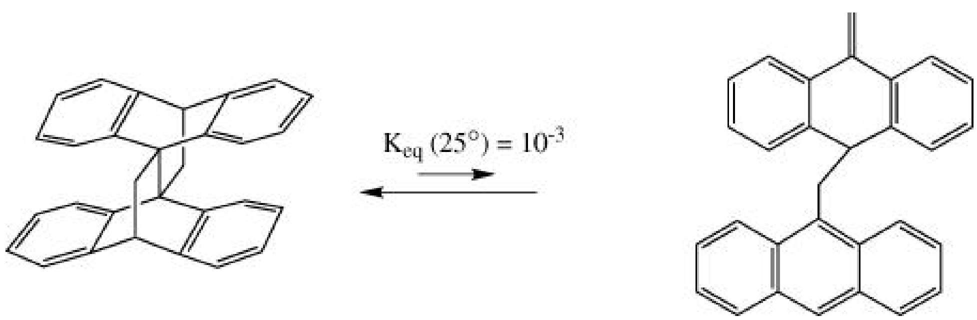


Although DA dimerization rates of a number of ketals have been determined, (382) no quantitative information on the rDA step is available.

Dimethylfulvene appears often in the rDA literature as the diene educt, but rarely as the dienophile. One of the exceptions is depicted. (385)

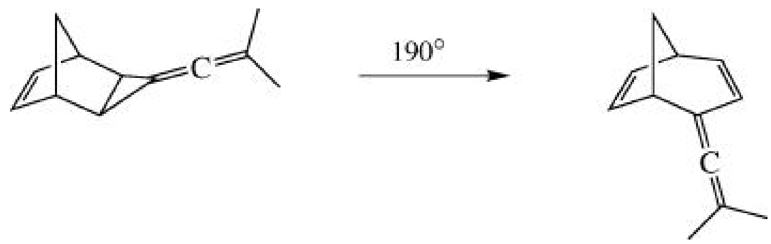


Lepidopterenes, the fascinating materials named for the butterflies they resemble, are formally intramolecular cycloadducts of anthracenes and 1,1-diaryl ethylenes. Although the adducts are strongly favored in ambient temperature equilibria, both the DA and rDA reactions are relatively facile. (386)

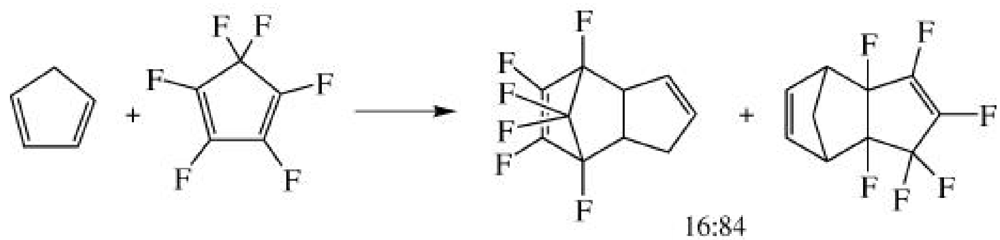


Substituents can appreciably affect the equilibrium position, generally leading to the cycloadduct being even more strongly favored. (387-389) These systems also exhibit interesting photochemistry, with evidence for formation of an exciplex intermediate. (389, 390)

A vinyl or aryl substituent on the embedded dienophile clearly lowers the activation energy for the rDA process, as already discussed. Not surprisingly, relatively few failures of attempted rDA reactions with substrates fitting this description have been reported. One such is easily explained by facile alternative rearrangement. (391)



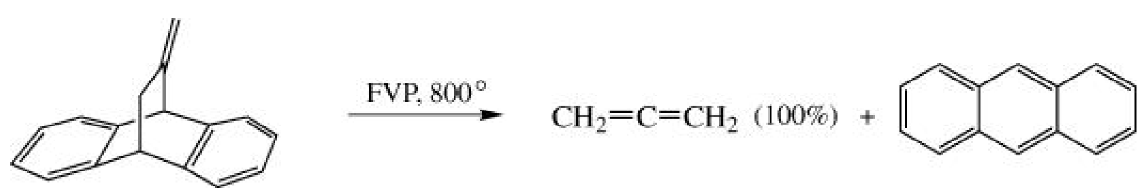
More puzzling is the claim that the ratio of products for the reaction of CP with perfluorocyclopentadiene $CP(F)_6$ is invariant with temperature (20° to 120°), and that the products do not interconvert or undergo Cope rearrangement. (392)



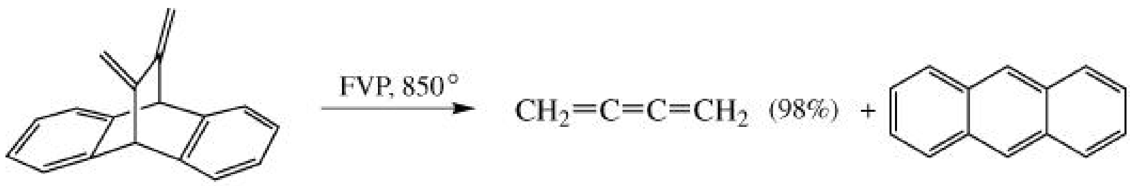
3.12. Allenes and Related Polyenes

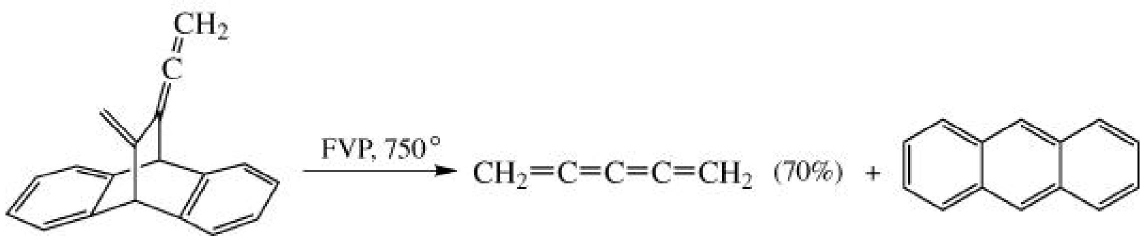
Allenes constitute a small but important subset of rDA products. Nearly all examples (see Table VIII) have been made by FVP methods, and relatively little can be said about comparative ease of reactions. Most of the nonfunctionalized allenes have been derived from anthracene cycloadducts.

Allene itself is formed in quantitative yield by the reaction shown. (393)

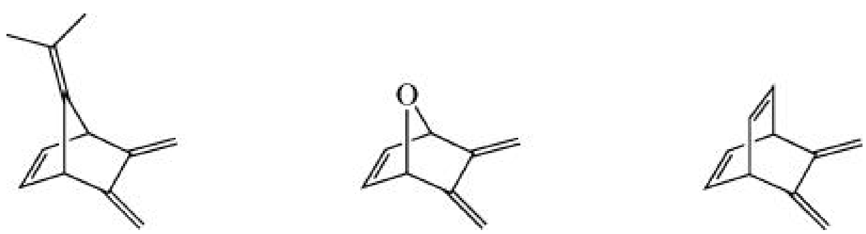


The higher homologs 1,2,3-butatriene and 1,2,3,4-pentatetraene have been generated in analogous reactions, both in relatively good yield, although the tetraene is more reactive and polymerizes at room temperature. (393, 394)

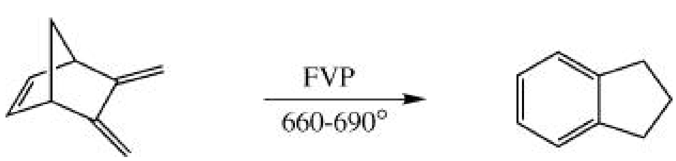




In addition to the anthracene adduct, the cycloadducts of dimethylfulvene, furan, and benzene illustrated below have, under FVP conditions, given 1,2,3-butatriene in yields of 2, 80, and 100%. (395)

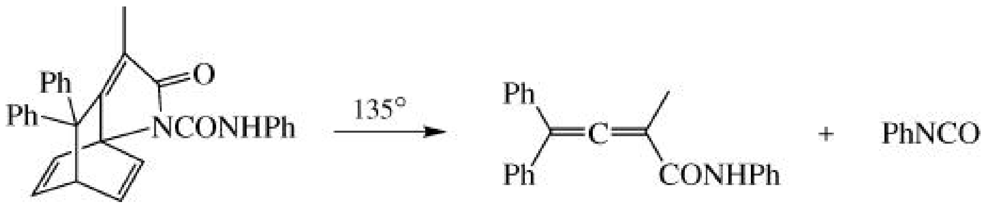


In marked contrast, the analogous CP adduct gives no rDA products, providing instead the rearrangement product hydrindane. (395)

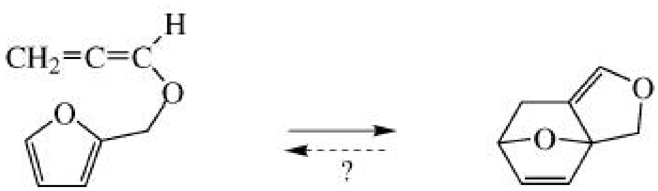


Allenes bearing either electron-withdrawing or -donor groups have been isolated from rDA reactions of both anthracene, and more commonly, furan adducts. The latter appear to be the more reactive, as judged by the lower FVP temperatures used.

Apparently only two intramolecular rDA reactions that generate an allenic dienophile have been demonstrated. (396) This reaction occurs at relatively low temperature, presumably because the “diene” is a benzene derivative (the N - Ph of the allenic product; the PhNCO coproduct may be formed by a retro-ene reaction).



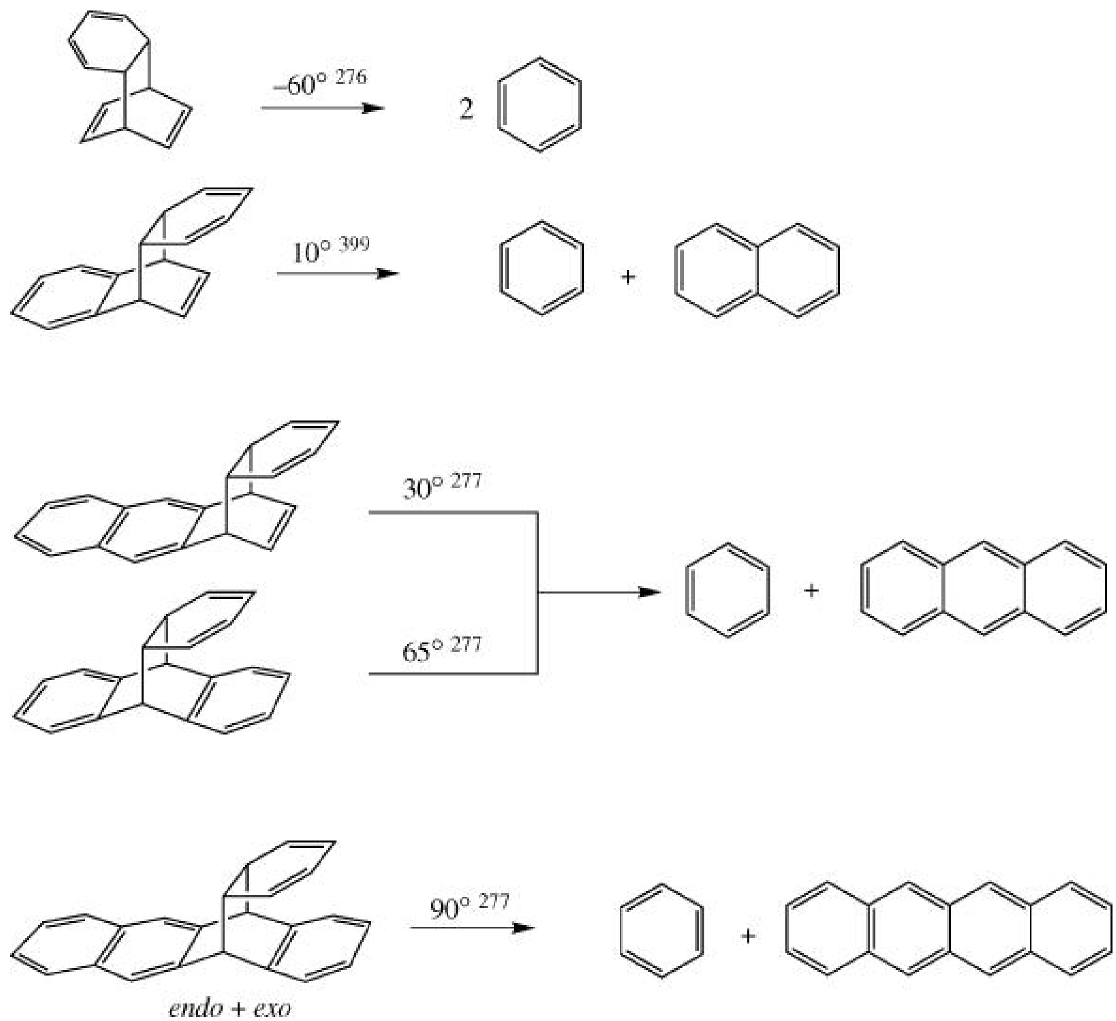
Although a furan-allene DA reaction of the general form shown has been depicted as reversible in several papers, (397, 398) no evidence has been presented to support the rDA step.



3.13. Aromatics and Heteroaromatics

This section and the corresponding Table IX focus on rDA reactions that generate simple carbocyclic aromatics (benzene, naphthalene, etc.) as the expelled *dienophile* component. A few heteroaromatic examples are included at the end of the table; the starting materials for these reactions are of a type commonly considered to be intermediates in reactions of olefins with 1,2,4,5-tetrazines, which typically occur by DA reaction followed by rDA loss of N_2. Many examples devoted to this reactive system are collected in a table in Part II of this review. Formal heteroaromatics in which the heteroatom is directly bonded to the dienophile carbon (e.g., furan) are also reserved for a later section of Part I.

The favored status of rDA reactions that generate resonance-stabilized products has already been pointed out. The kinetics of several systems have been studied. These examples with activation parameters or similar data are shown in Table IX. Rate enhancement is associated with aromaticity of either dienophile or diene component, and is reinforced when both educts are aromatic. The reaction rates are qualitatively related to the added resonance stabilization energy of the products. This feature is illustrated by the temperatures needed to observe facile rDA reactions in the following examples:

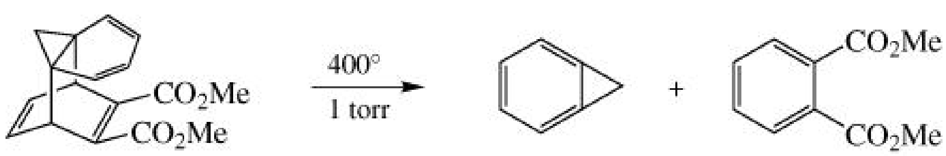


In this context, it is interesting that the “aromatic” character of a substituted furan may be evoked from the relatively low temperature needed for the rDA reaction leading to benzene and isobenzofuran. (400)

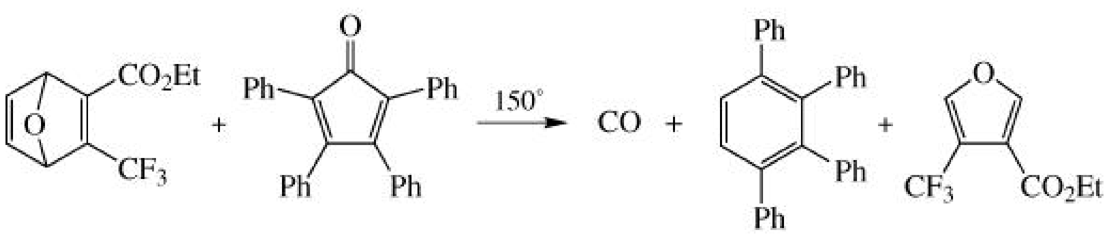
However, the analogous reaction to form CP as the diene component also occurs readily under very mild conditions. (174, 280)

Both the benzene ring (dienophile) (401) and the CP (402) may bear simple alkyl/aryl substituents without impeding the rDA reaction, but with $CP(Cl)_6$ as the expelled diene more forcing conditions (135°) are required. (174) Tetrachlorination of the benzene ring, conversely, has little effect on the temperature (35°) needed for rDA reaction. (403)

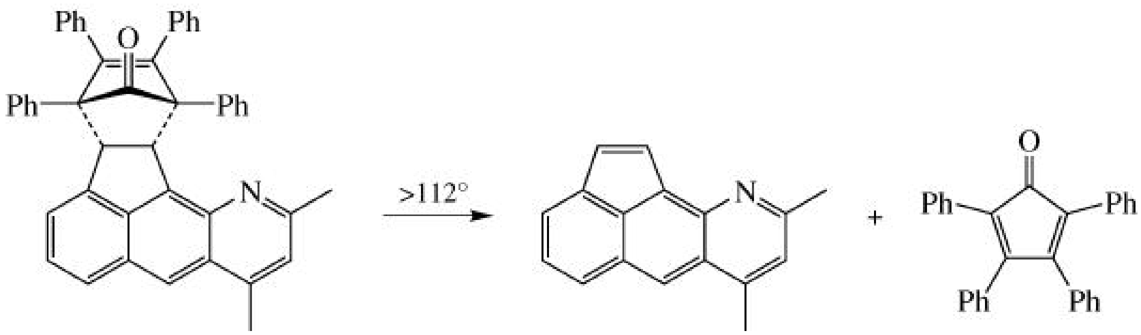
Benzocyclopropene has been formed by an rDA reaction that takes advantage of both educts being aromatic, although the reaction was carried out under FVP conditions (as shown) that do not allow ready comparison with other reactions. (404) Similar conditions were used to prepare 1,2-naphthocyclopropene. (405)



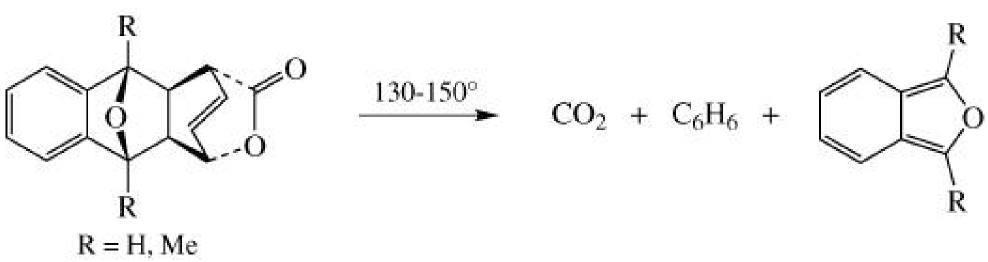
The very facile low-temperature reactions described in this section involve starting materials that are generally nontrivial to prepare, as one might expect. More commonly for synthetic applications, the same overall result may obtain from higher-temperature (130–160°) reaction of an olefin with a substituted cyclopentadienone. These processes involve sequential DA, decarbonylation, and rDA reaction; an example (one of many) is illustrated. (406)



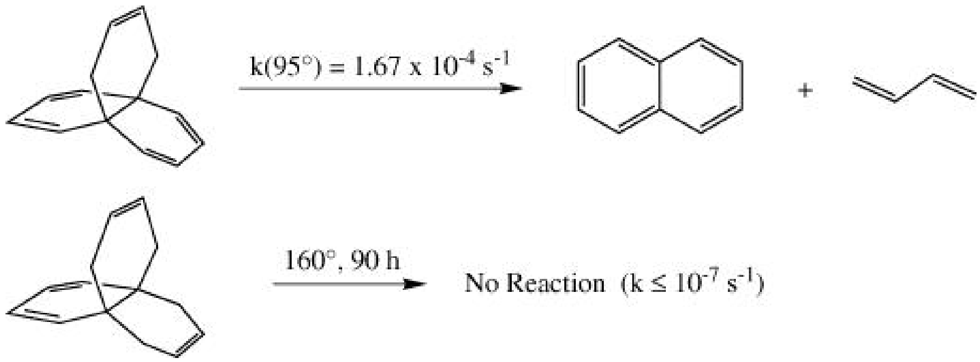
With sufficiently reactive starting dienophiles the bicyclo[2.2.1]heptan-7-one can be isolated by carrying out the initial DA reaction at temperatures £110°. While decarbonylation is the characteristic reaction of these products, the reverse rDA reaction to regenerate the cyclopentadienone is also known. In the example shown here, this "nonproductive" rDA reaction is favored both by the aromatic character of the dienophile and the increase in steric crowding that would result from decarbonylation. (407)



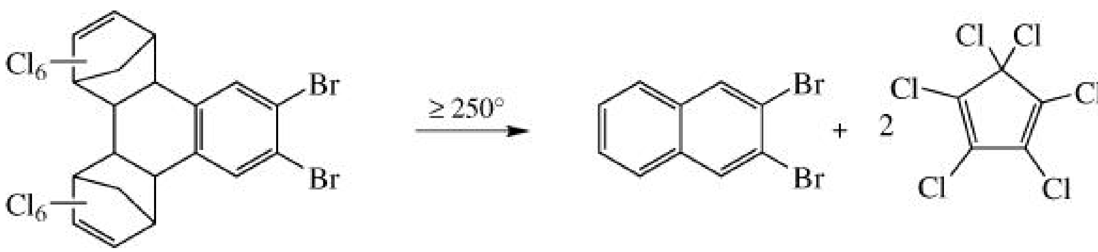
A similar reaction and intermediate arises in the chemistry of α -pyrone. (400,408) In these reactions, the loss of CO_2 constitutes a formal rDA step (the first of two in the sequence). A table in Part II of this review is devoted to the extensive rDA applications of α -pyrone, but a few examples are included in Table IX for comparison with closely related processes.



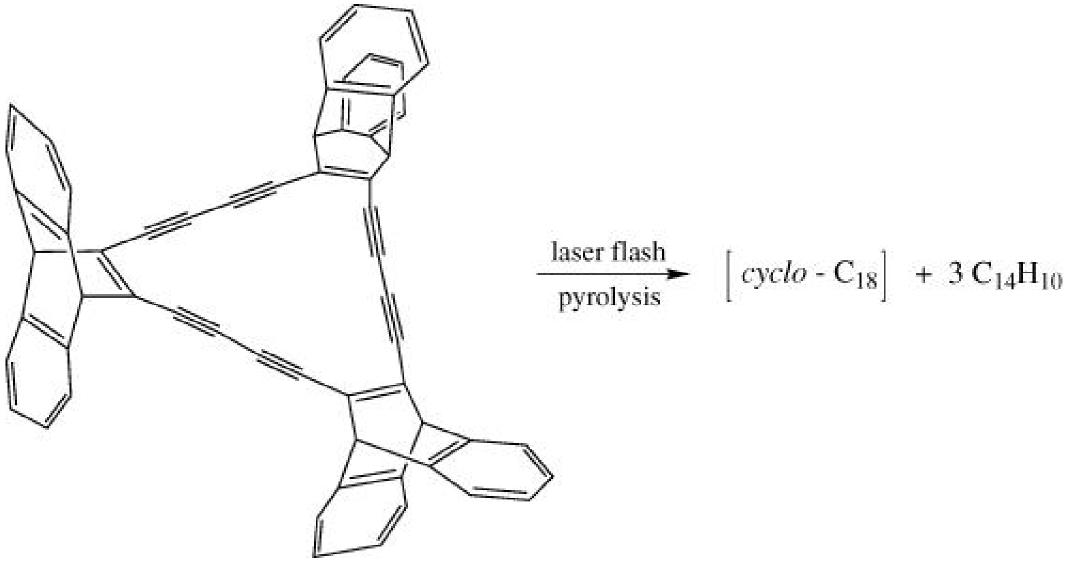
Reactions that generate naphthalenes as the dienophile component have both theoretical and practical applications. It is interesting that the expulsion of butadiene to form naphthalene as shown occurs at 95° (note that except for modest diene resonance effects, the entire stabilization energy of naphthalene is developed in this reaction), whereas the analogous reaction to generate a substituted benzene is not observed even at much higher temperature.



Some substitution patterns in naphthalene cannot be prepared directly by classical electrophilic substitution, e.g., 2,3-dihalonaphthalene. An alternative route was discovered with the finding that $CP(Cl)_6$ will serve as a diene to give the 1,2::3,4-bis adduct in a double DA reaction. The product of this reaction then tends (often strongly so) to undergo electrophilic substitution at the sites remote from the bicyclic rings. After rDA reaction, the $CP(Cl)_6$ is regenerated along with the desired 2- or 2,3-substituted naphthalene, as illustrated. (411) Several substitution patterns are described in the literature (frequently without yields), and these are reproduced in Table IX. (412) The major drawback of this sequence is the relatively high temperature needed for the rDA step, typically 250–400°.

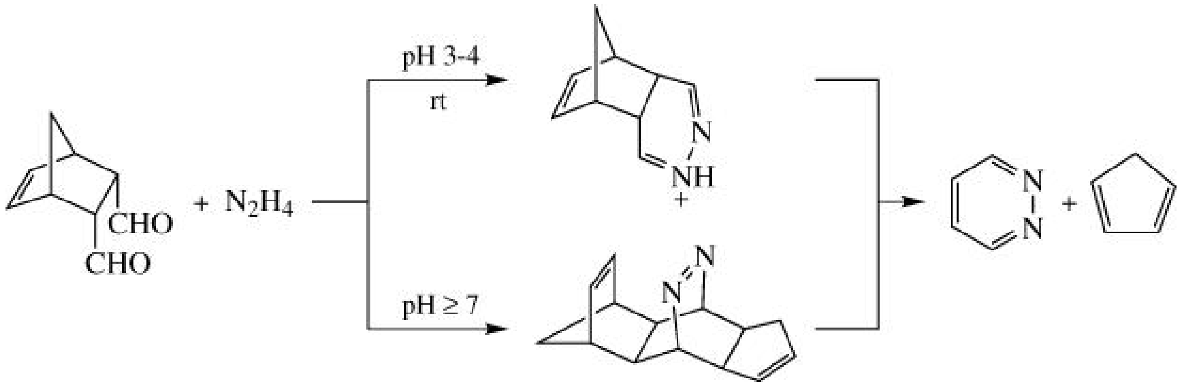


One of the more exotic “aromatic” systems that has been generated (as a reactive intermediate) is *cyclo*-C_{18}, reportedly formed by laser flash pyrolysis of the tris(anthracene) cycloadduct shown. (413, 414) This interesting product qualifies by simple electron count as a Hueckel aromatic (4n + 2; n = 4).

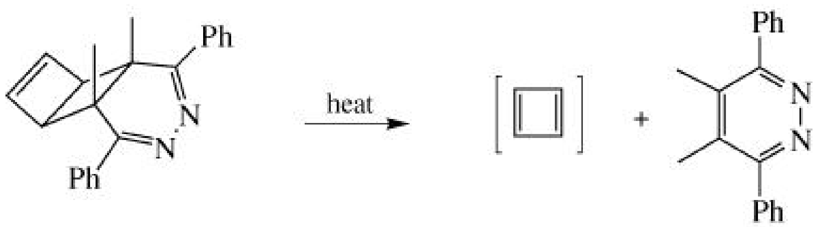


C_{60} (buckminsterfullerene) is quite reactive as a dienophile in DA reactions, being similar to NMM. (415) DA reactions were among the first examined with this intriguing molecule, and several cycloadducts have been described. The view that rDA reactions of C_{60} adducts are relatively facile is also widespread among workers in the field, (416) although carefully controlled experimental work on this question has been limited. The DA adducts that have been described and the conditions of claimed rDA reactions are as follows: CP (³95°) (417-421); 2,3-dimethylbutadiene (room temperature) (419); 1,3-diphenylisobenzofuran (room temperature) (419); anthracene(³60°) (419, 420, 422); butadiene (³100° by thermal gravimetric analysis) (420); $CP(Me)_5$ (³160° by TGA; ³200°). (420, 421) Superconducting material thought to be Rb_3C_{60} has been formed by the thermolysis of $Rb_3C_{60}CP(Me)_5$, at 250° for 2+ days. (420)

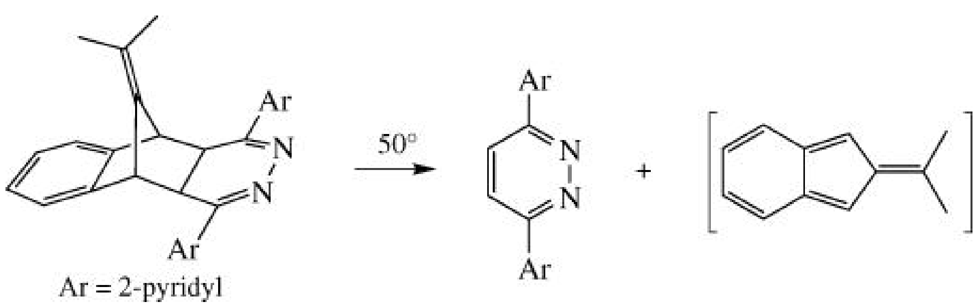
The reaction of a substituted succinaldehyde with hydrazine provides simple entry to the dihydropyridazine ring system. When applied to the *endo* dialdehyde shown, interesting pH dependence is observed. (197) Under acidic conditions rapid rDA reaction occurs to give pyridazine and CP. Under neutral/basic conditions, the CP formed from an apparently slower rDA process is trapped by the dihydropyridazine to give the tetracyclic product shown; on treatment with acid this species undergoes double rDA reaction.



Dihydropyridazines can also be isolated from the DA-rDA reaction of an olefin with a tetrazine (commonly a 3,6-diaryltetrazine is used). An interesting application is shown, which gives cyclobutadiene. (423) As pointed out earlier, the unique symmetry of cyclobutadiene allows this scission to be viewed as either a r[2 + 2] or rDA reaction.



Dimethylisobenzofulvene has been generated by similar formation of a heteroaromatic. (424)

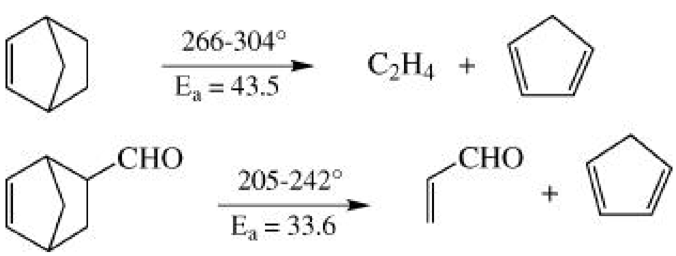


An attempt to generate the parent isobenzofulvene by a similar reaction sequence failed, as did a pathway based on decarbonylation-rDA methodology. (425) Isobenzofulvene remains an unconquered synthetic challenge.

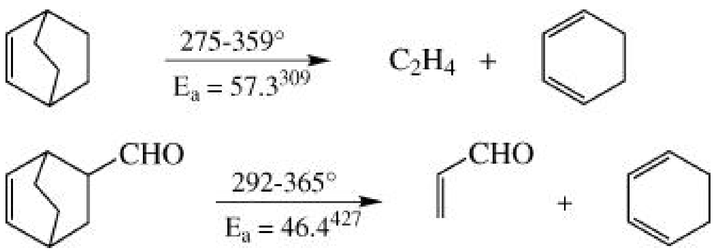
3.14. Mono-Electron-Withdrawing-Group (EWG)-Substituted Alkenes

Table X contains the extensive compilation of rDA reactions that eject an olefinic dienophile bearing a single EWG. The order of presentation is by increasing atomic number and oxidation state of the EWG, with a secondary effort made to retain the subgrouping of the common diene component. Thus the Table first treats EWG= imine (only two entries), followed by EWG = CN (numerous examples, grouped by diene component e.g., CP, aromatics (anthracene, furans, etc.). The progression is to EWG = carbonyl (aldehydes and acyclic ketones, followed by cyclic ketones— including cyclopentadienones— in order of increasing ring size), thiocarbonyl, and then to higher oxidation states: amides, esters, lactones (exocyclic followed by endocyclic double bond), homo-rDA examples, acid chloride (one possible example), and finally thioamides.

With this section we reach the realm of “reactive” dienophiles, in the context of common electron demand LUMO dienophile DA reactions. How do EWG groups affect the rates of rDA reactions? There has been surprisingly little quantitative work in this area, but it is clear that the introduction of an EWG directly bonded to the embedded dienophile substantially lowers the activation energy for the rDA reaction. Consider, for example, the adducts that give rise to CP plus ethylene (292) or, respectively, acrolein. (426)



Another comparison of these two dienophiles is provided by the rDA reactions that form cyclohexadiene as the common diene component; again, appreciable lowering of the activation energy is associated with inclusion of the CHO group.

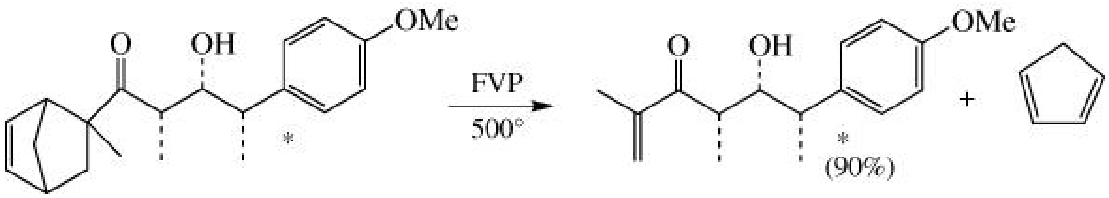


Already included in a table in the Mechanism section, the effects of common EWG groups on the rDA rates of anthracene adducts bear repeating here (k_{rel} values follow the EWG for the reaction depicted): (175)

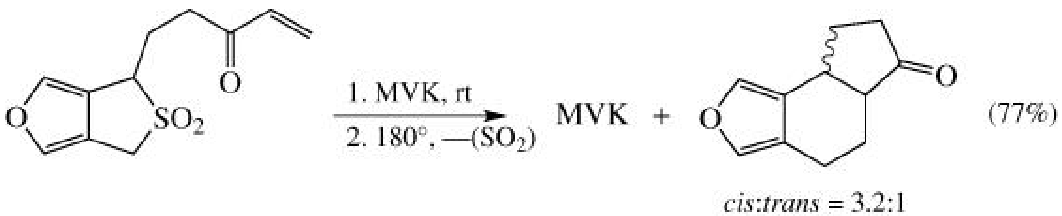
CHO (251); Ac (179); CO_2H (139); CN (76); E (56); $CONH_2$ (33); NO_2 (17); (H = 1).

The CHO group exerts the largest effect of the EWGs in the anthracene series. This rate factor (251 relative to H) is appreciable, but certainly larger substituent effects are known in organic reactions. It has not been established whether this order of reactivity would hold for a different diene series, although portions are reproduced in a similar reaction involving 9-(2-pyridyl)anthracene as the diene. (177)

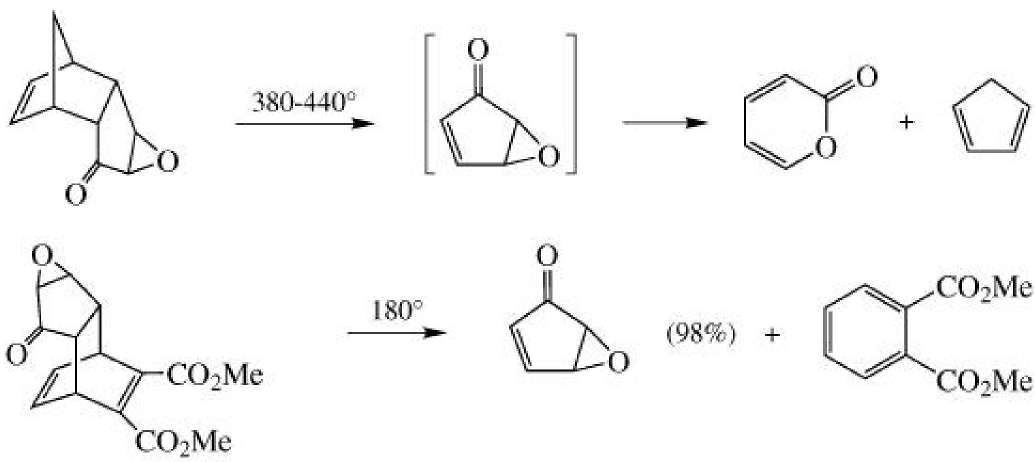
Although an EWG clearly activates an adduct toward rDA reaction, many or most useful synthetic procedures ofter utilize very high temperature methods (flash vacuum pyrolysis, FVP) that mask the inherent activation energies. Numerous examples of preparation of α , β -unsaturated ketones, both acyclic and cyclic, are shown in Table X. An example in which a sensitive optically active enolizable ketone is formed is illustrative. (428)



An interesting application of methyl vinyl ketone (MVK) in a presumed DA-cheletropic-DA-rDA one-pot sequence has been reported. (429)

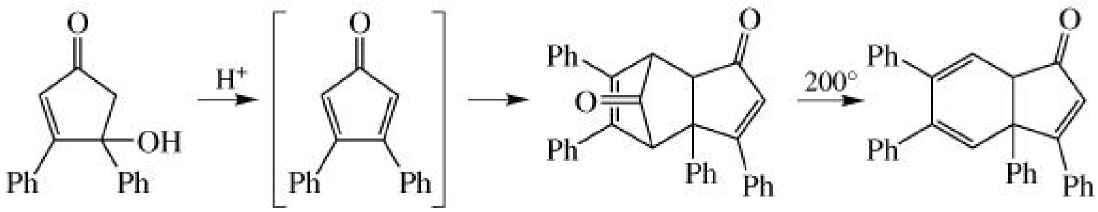


The α, β -epoxy ketone functionality is thermally sensitive, although it has been reported to survive intact in some rDA reactions that generate cyclopentenones. (430-432) For example, the temperature needed to effect rDA reaction of the CP adduct causes rearrangement to α -pyrone, (431) whereas the much lower temperature needed for the aromatic derivative allows isolation of the epoxy ketone in 98% yield. (431)



Efforts to moderate the rearrangement to the α -pyrone by ketalization of the carbonyl group in the starting adduct have met with some success, for EWG-substituted derivatives. (430, 432, 433) Examples are included in Table X along with the related ketones, for ease of comparison.

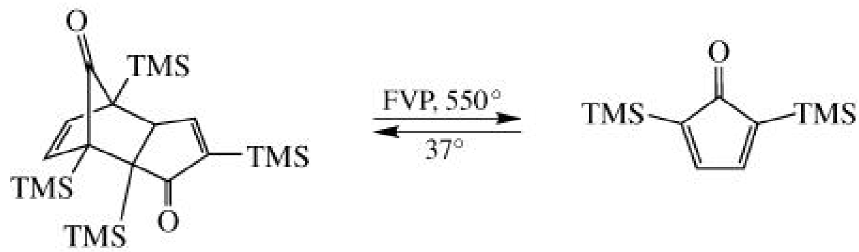
Cyclopentadienone and its derivatives have attracted the attention of many chemists over the years. As previously noted, probably the first example of an (unrecognized) DA reaction was described in 1887 by Japp and Burton. (10) Thermal dehydration of the aldol condensation product of acetone and benzil gave 3,4-diphenylcyclopentadienone, which underwent very rapid DA dimerization; another first for this work was recognition of the thermal loss of CO, the first cheletropic reaction.



Cyclopentadienone itself is extremely reactive in DA dimerization, but it is nonetheless a thermodynamically respectable material, as shown by isolation at –196°, a temperature at which it is "indefinitely stable". (434) FVP of *o*-benzoquinone, either directly or of a cheletropic reaction precursor, proved effective for formation of this once very elusive species. (434) *o*-Benzoquinone has also been generated as the intermediate in a rDA process, with subsequent formation of cyclopentadienone (isolated as dimer in this instance). (23)

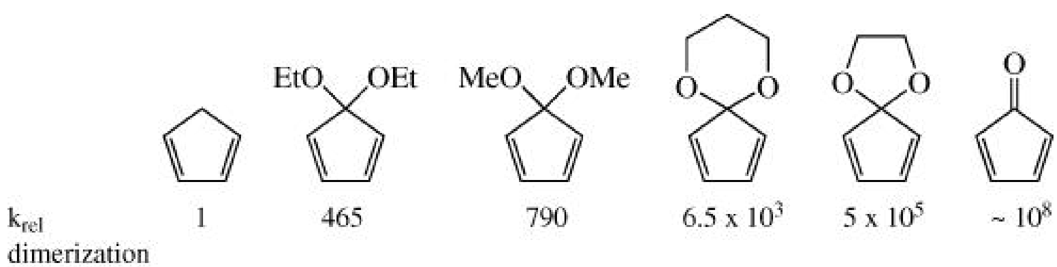
It has long been recognized that both the rate of DA dimerization and the stability of the cycloadduct are diminished by substituents, although mostly these conclusions are based on qualitative observations. There is a considerable body of literature on substituted cyclopentadienone dimers, and the topic has been reviewed. (89) With the early focus on preparation and dimerization, information on the reverse reaction tends to be in the form of casual observations (e.g., colorless dimer gives red solution).

Tetrasubstituted derivatives are either more stable (tetraaryl) or at least isolable as monomers (2,5-dialkyl-3,4-diaryl) at ambient temperature; the best known example is commercially available tetraphenylcyclopentadienone ("tetracyclone"), which is not known to dimerize. Trisubstituted (various 2,3,5-, and 2,3,4-triphenyl) derivatives prefer the dimer structure as solids, but dissociate easily in solution. Disubstituted cyclopentadienones prefer to exist as dimers; this is true even of 2,5-bis(trimethylsilyl)cyclopentadienone, which can be isolated (cold trap) by FVP of the dimer, although dimerization occurs readily on warming. (435)

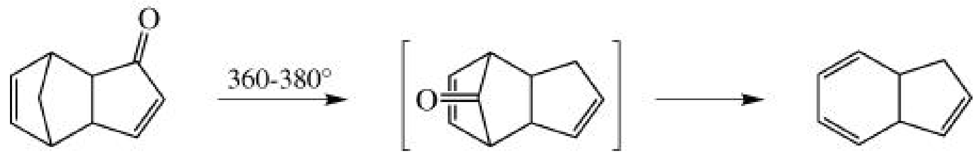


Even 2,4-di-*tert*-butylcyclopentadienone dimerizes at 25°, although at an easily measurable rate ($k = 2.4 \times 10^{-5}\ M^{-1}\ s^{-1}$). The bulky 2-alkyl group, as one would expect, exerts the greater influence on rate, since the monosubstituted analog 3-*tert*-butylcyclopentadienone dimerizes "at least 10^7 times faster." The rDA reactions were not studied. (436)

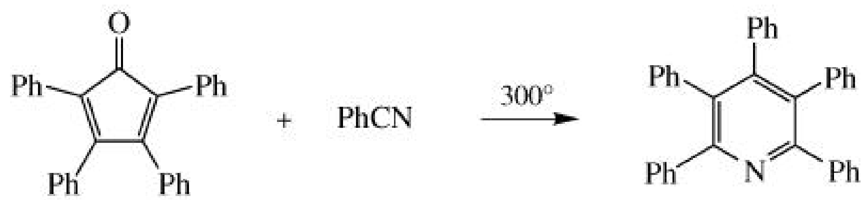
DA dimer reactivity can also be moderated by derivatization of the carbonyl group, and DA dimerization k_{rel} values for the following compounds have been estimated. (382, 383) Unfortunately, with the exception of cyclopentadiene dimer (already discussed), there is no information on rDA rates of these dimers.



Cyclopentadienones may serve as either dienophile or diene in reaction with other DA-active counterparts (and of course both roles are fulfilled in dimerization). In fairly early work, the adduct of CP(diene) and cyclopentadienone-(dienophile) was shown to give, on pyrolysis, the decarbonylated product expected of the rearranged isomer, in which diene and dienophile roles have been formally reversed. This rearrangement could occur either by rDA/DA reactions, or by [3 + 3] reaction of the *endo* adduct. (437)

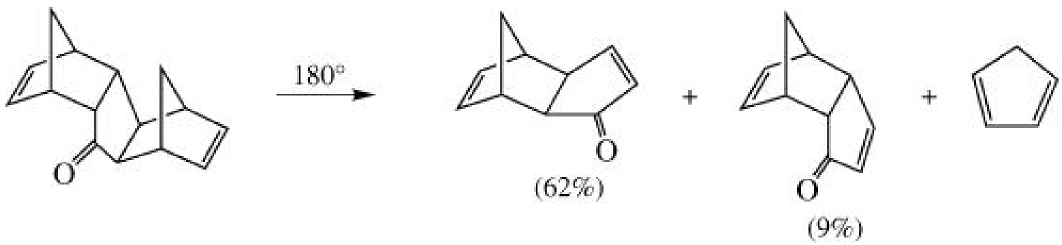


Much of the useful synthetic chemistry of cyclopentadienones involves the tetraaryl derivatives, which tend to act as dienes, leading to bicyclic adducts that undergo cheletropic loss of CO. When acetylenic dienophiles are employed, the product is the corresponding tetraaryl benzene derivative. Even a nitrile can serve as dienophile in an analogous reaction, as shown in this early (1935) example. (438)



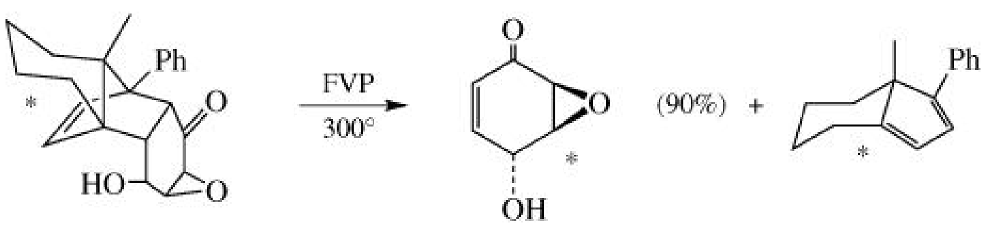
With olefinic dienophiles, the products after decarbonylation are dihydroaromatics, which with appropriate substitution give rDA reactions to form tetraarylbenzenes and new, often difficulty accessible, dienes. Some reactions have been described in the context of Table IX. While decarbonylation occurs more or less readily depending upon substituents, trivial rDA reactions may occur in competition with this desired pathway. For example, the reaction of tetracyclone with acrylonitrile gives DA adduct reversibly; decarbonylation was effected in this instance by continued heating in excess acrylonitrile. (439) Reversible formation of the tetracyclone (diene)-CP (dienophile) adduct has also been noted. (440)

Cyclopentadienone forms a bis-adduct with CP; the *endo-anti-exo* adduct on heating gives a mono-rDA product ratio *exo*/*endo* = 7, indicating that the *endo*-fused CP is more readily removed. (441)



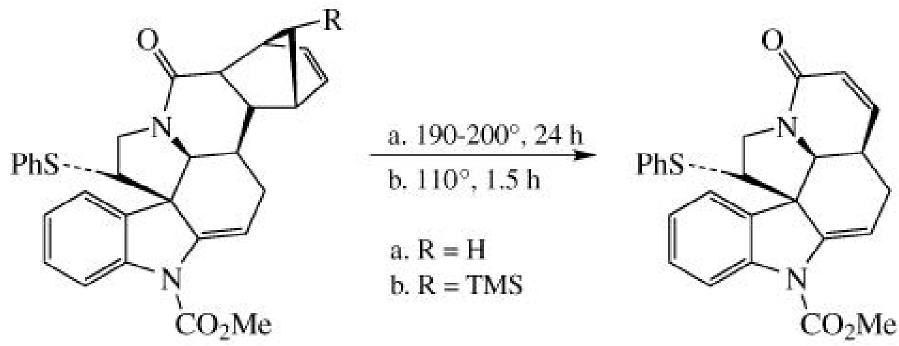
Similar results are obtained in the $BF_3 \cdot Et_2O$ catalyzed reaction, which occurs at room temperature. (217)

Numerous α -methylenecyclopentanones, 2-cyclopentenones, and 2-cyclohexenones have been prepared by rDA reactions of cycloadducts with most of the commonly employed dienes, as depicted in Table X. These reactions include several optically active examples. The active adducts have been prepared in several classical ways (resolution), and more recently through the use of the novel optically active CP derivative (Winterfeldt's diene). This useful diene is regenerated cleanly in thermal rDA reactions, which can be used to generate rather sensitive dienophile educts, as illustrated. (442)



The diene exhibits high regio- and stereoselectivity in many DA reactions, and has been used in several syntheses. It appears to be limited only by modest reactivity (requiring an activated dienophile), and to a lesser extent by the relatively high temperatures needed for rDA reaction. It should be noted that several similar (racemic) products have been generated by thermal rDA reactions of the analogous dimethylfulvene adducts, which decompose in the 140–180° range (see Table X).

Five- and six-membered α , β -unsaturated lactams (including several thymine analogs) have been prepared by rDA reactions. The rDA activating influence of the trimethylsilyl group on CP was first noted in the synthesis of a lactam. (258)



In addition to unsaturated esters, α -methylene- β - and γ -lactones, and α , β -unsaturated γ -lactones have been common synthetic targets for rDA procedures, as shown by many entries in Table X. Thia and thiono analogs have also been generated.

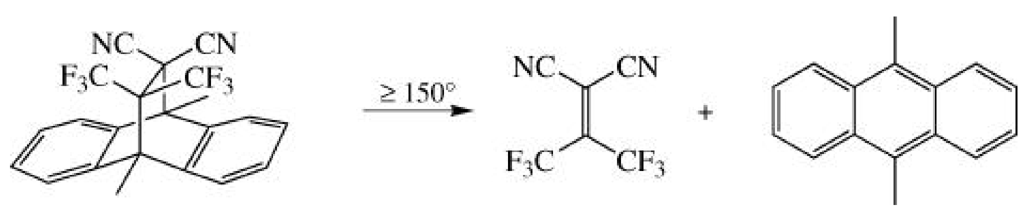
3.15. Di-EWG Substituted Alkenes

To simplify access, this very large class of rDA reactions has been divided into six subcategories of dienophile educts: 1,1-; acyclic 1,2-; cyclic 1,2-; quinones; maleimides; and maleic anhydrides.

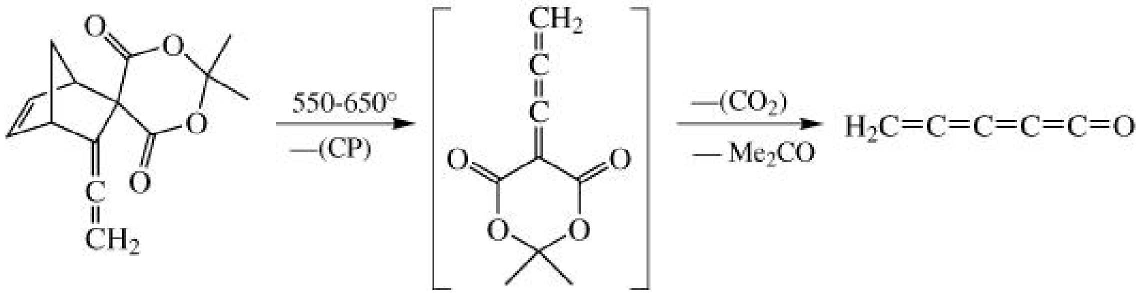
3.15.1. 1,1-Di-EWG Substituted Alkenes

These important and very reactive monomers, which are susceptible to Michael additions, polymerization, and cycloaddition reactions, have been conveniently accessed by rDA methods. Both simple thermal reactions and FVP procedures have been employed, and the usual range of embedded dienes is represented, as shown by the entries in Table XI-A. A representative example, in which MA is used to prevent back reaction, has been discussed in the context of scavenger use. (265)

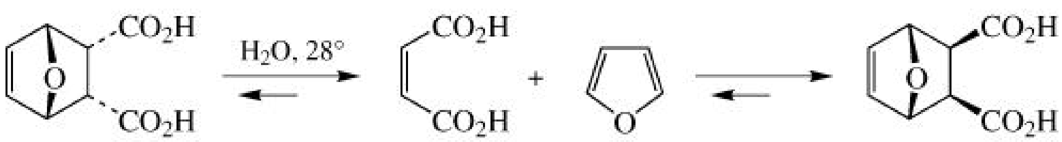
Following the formalism adopted for this review, the very reactive dienophile in the next equation is listed in this category, (443) although its DA reactivity suggests that it is comparable to the tetra-EWG substitued alkenes, treated in a later section.



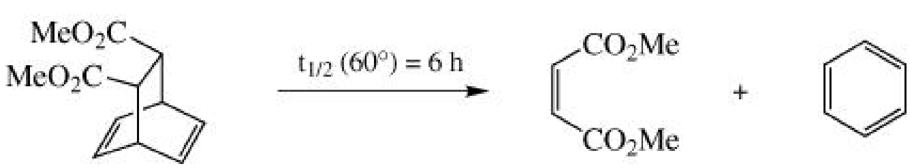
Several of the dienophiles described in Table XI-A have proven to be too reactive to isolate. (187) These include proposed intermediates that decompose further to form ketenes and their derivatives. (444)



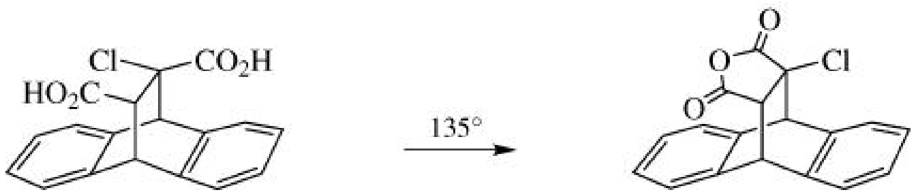
3.15.2. Acyclic 1,2-Di-EWG Substituted Alkenes
The expected stereochemistry is found in the examples of rDA reactions that generate maleic and fumaric acids and their derivatives (e.g., esters). These reactions tend to occur at relatively modest temperatures. Thus, the *endo*-maleic acid adduct of furan is difficult to prepare, (445) and is converted to the *exo* adduct at 28° upon dissolution in water. (446)



Similarly, the dimethyl maleate-benzene adduct fragments readily on mild heating. (284)



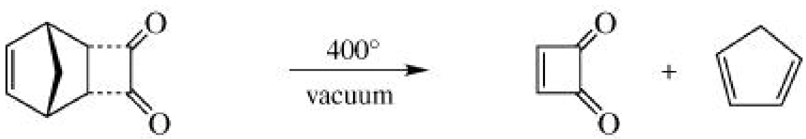
Most anthracene adducts give products of expected stereochemistry, and several examples are included in Table XI-B. Some apparent anomalies in earlier DA studies may involve rDA-rearrangement-DA steps, (447, 448) although acid catalyzed epimerization may also account for these observations. (447)



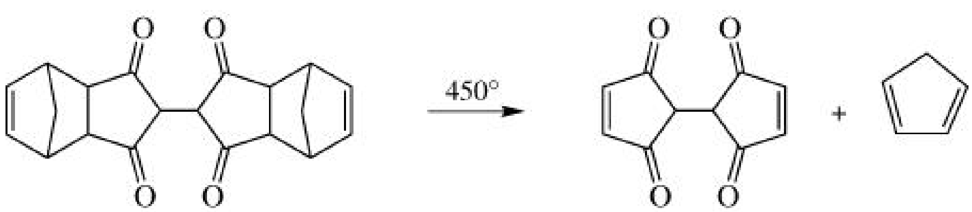
3.15.3. Cyclic 1,2-Di-EWG Substituted Alkenes

The large number of rDA reactions that fall under this general classification have been further subdivided into reactions that generate miscellaneous 1,2-di-EWG-substituted cycloalkenes (the focus of this section and Table XI-C), followed by sections (and Tables XI-D, -E, and -F) on quinones, maleimides, and maleic anhydrides.

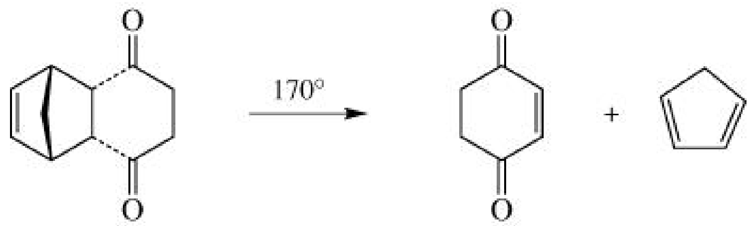
Cyclobut-3-ene-1,2-dione has been generated by vacuum pyrolysis of both the CP and anthracene adducts. (449)



Although the simple five-membered homolog apparently has not been prepared by rDA methodology, an interesting bis-analog has been described. (450)

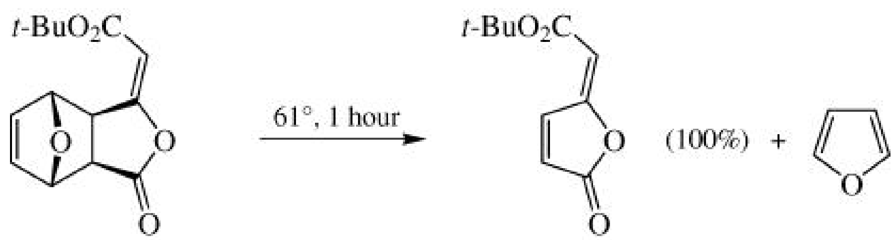


The six-membered homolog is especially interesting in that this isolable enedione is a tautomer of hydroquinone, providing one of many examples of successful application of rDA reactions to the formation of metastable products. (451, 452)

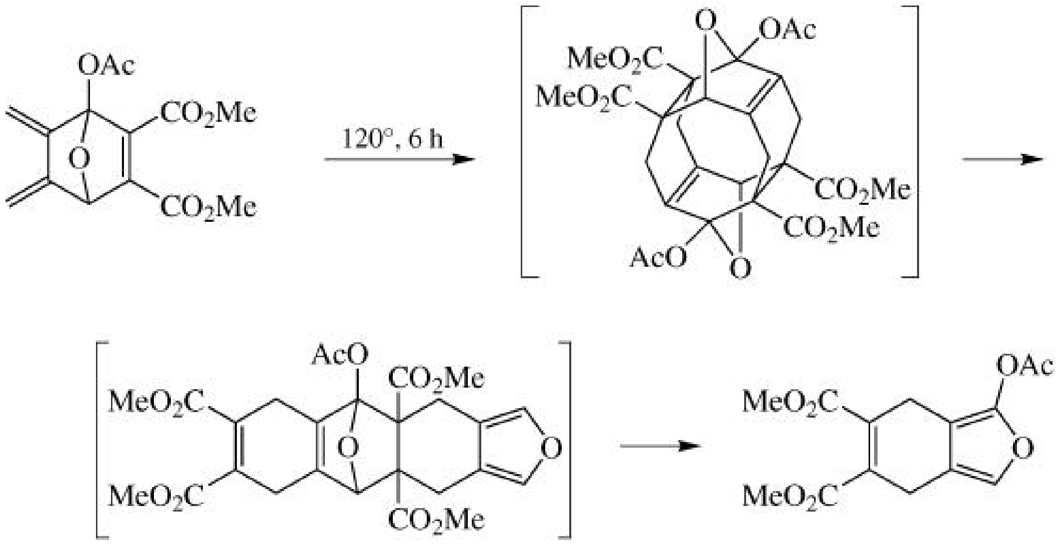


Several alkylated derivatives have been prepared by analogous reactions, but phenyl substitution causes facile tautomerism to 2-phenylhydroquinone. (451)

The MA cycloadducts of common dienes (in contrast to MA itself which is reported to polymerize) react with stabilized Wittig ylides to form conjugated methylene lactones. These adducts give system-dependent stereochemistry when heated, as illustrated by the furan derivative, which undergoes rDA reaction on warming. (453)



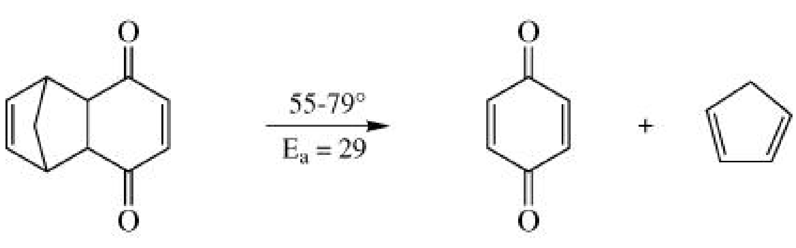
An unusual (diene + dienophile) starting material gives a nontrivial product, among others, when heated. A mechanism has been proposed that involves formation of the cyclic bis-adduct, which can then form this product by two successive rDA steps, neither being the reverse reaction of the original DA cycloaddition. (454)



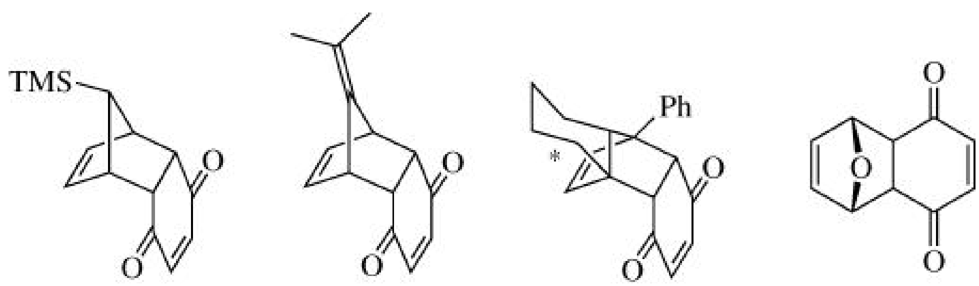
The norbornadiene and 7-heteroatom analog cycloadducts of common dienes and acetylenic dienophiles react readily with dipolar reagents to give [2 + 3] cycloadduct that more or less readily undergo rDA reactions. In most instances (see Table XI-C) mixtures of products result, but some reactions show considerable selectivity. An example is the reaction with dimethyldiazomethane. (455)

3.15.4. Quinones as Dienophiles

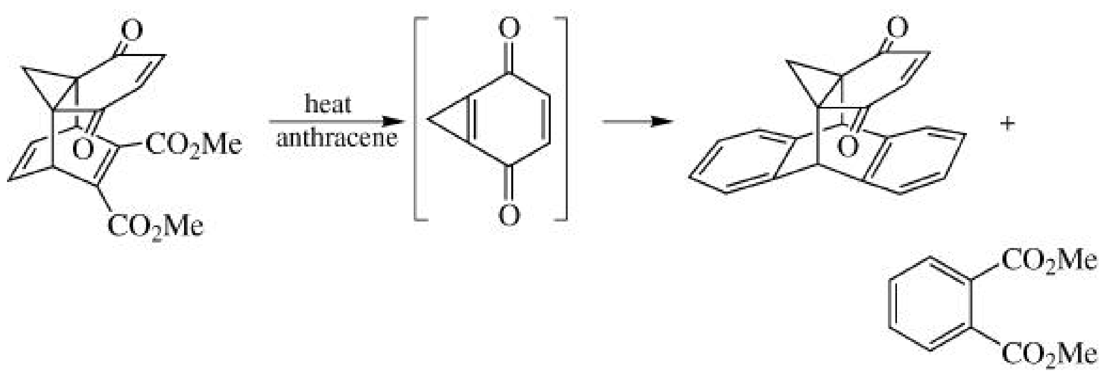
Benzoquinone itself has been generated in several rDA reactions, and formation from the CP adduct was one of the earliest such reactions studied in some detail. (259) The *endo* stereochemistry of the adduct was not demonstrated in this early work, but is assumed based on later work and many related examples.



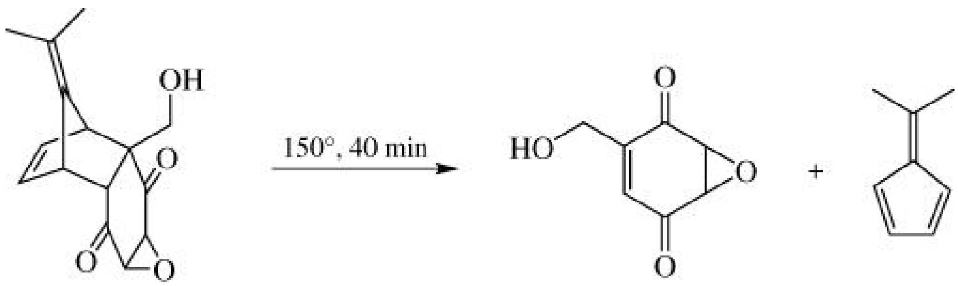
As noted previously, a trimethylsilyl substituent enhances rDA reactivity (E_a = 25). (258) Both the *endo* dimethylfulvene adduct (456) and the chiral Winterfeldt adduct (457) decompose at room temperature. The furan adducts of benzoquinone require high pressure for preparation, and both the *endo* and *exo* isomers decompose at 1 atm, at low temperatures (–8° and 5°, respectively). (458)



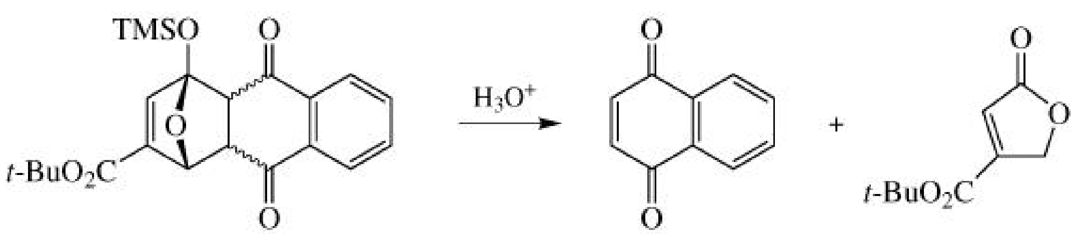
A highly strained cyclopropene quinone analog has been generated by the rDA reaction illustrated, as shown by trapping (in low yield) with anthracene as the in situ scavenger. (459)



Although technically belonging to the preceding section dealing with cyclohexenediones, several highly functionalized derivatives of the dimethylfulvenequinone adducts, both *endo* and *exo*, have been prepared and subjected to rDA reactions. These include systems that lead to natural products. Examples are found in Table XI-C, but some have been included in Table XI-D in order to provide a more direct comparison with the basic quinone substrates. The differences in reactivity are noteworthy. Whereas the *endo* quinone adduct decomposes near room temperature as noted above, the highly functionalized *endo* derivative lacking the double bond requires a temperature of 150° (the *exo* analog 170°), (460) still modest in comparison with many rDA processes.



A novel naphthoquinone adduct undergoes a room-temperature hydrolytic reaction in aqueous acid, analogous to a simpler reaction described in the section on acid catalysis. Presumably the silyl ether is hydrolyzed to the bridgehead hydroxy acetal (an unknown class of compounds), which then decomposes by a facile rDA reaction. (205)

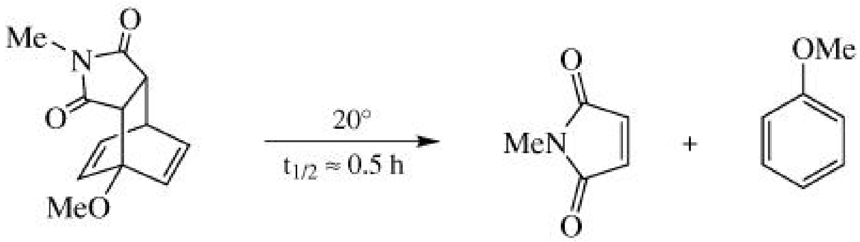


3.15.5. Maleimides

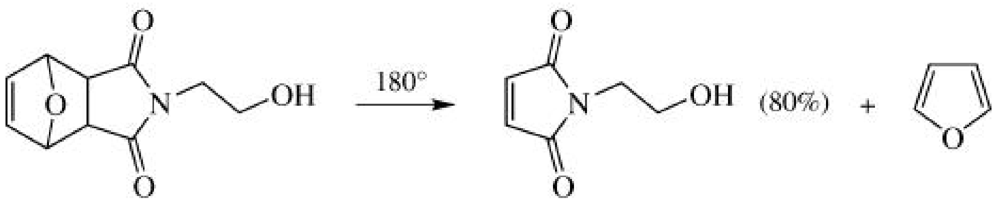
Maleimide and its *N*-methyl (NMM) and *N*-phenyl (NPM) derivatives have been extensively used as dienophiles in DA applications. NMM and MA react at similar rates with a range of dienes, but the NMM (and similar maleimides) are considerably more stable (3–4 kcal/mol) than the MA analogs. (267) This feature is useful for study of rDA reaction rates of cycloadducts that would otherwise be difficult to measure because of unfavorable equilibria.

The entries in Table XI-E show that the usual rDA relationship holds for common dienes, to the extent that these have been examined, with diene (approximate temp) following the order: anthracene(est. >210°); CP (200°); and furan (40°). The *N*-methylisoindole-NMM adduct undergoes rDA reaction at ~60° (or room temperature with $LiClO_4$ catalysis), (220) whereas the analogous isobenzofuran adduct is relatively stable at temperatures below 132°. (267) *Exo* cycloadducts are more thermally stable than *endo* isomers for all the bicyclo[2.2.1]heptane analogs that have been examined, a feature shared with the corresponding MA adducts.

The bridgehead methoxy group of the anisole-NMM cycloadduct presumably leads to appreciable rDA rate enhancement, an effect that is counterbalanced by the stabilizing influence of NMM, with the net result being reactivity that barely allows room-temperature isolation. (285)

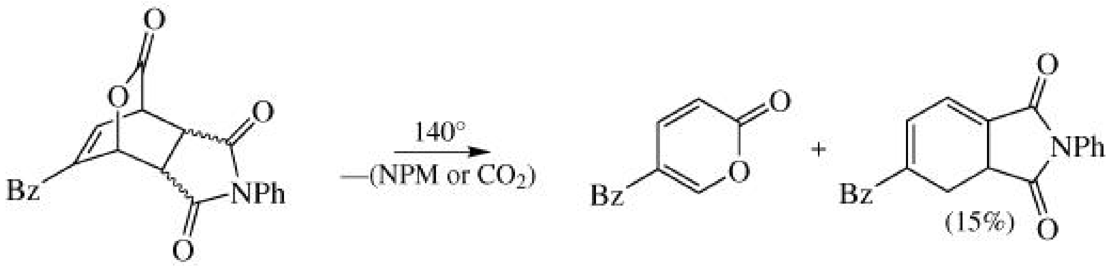


Higher temperatures than needed to effect measurable reaction are commonly used to drive off the volatile diene product and prevent back reaction, as in the synthesis of maleimide itself from the furan cycloadduct. (461) Analogous rDA reactions have been used to prepare a variety of N-substituted maleimides that contain reactive or biologically interesting functional groups. A simple example is shown. (462)

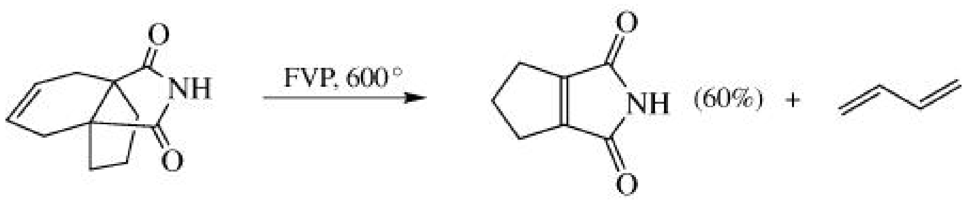


The useful *N*,*N*¢-bis(maleimide) has similarly been prepared from the bis(-furan) adduct. (463)

Cycloadducts of α -pyrone are usually of interest because of their propensity to undergo more-or-less facile rDA loss of CO_2 (topic covered in a later section), but the simple rDA reversal of adduct formation has been observed in several instances. An example in which these two competing rDA reactions are both observed is shown. (464)



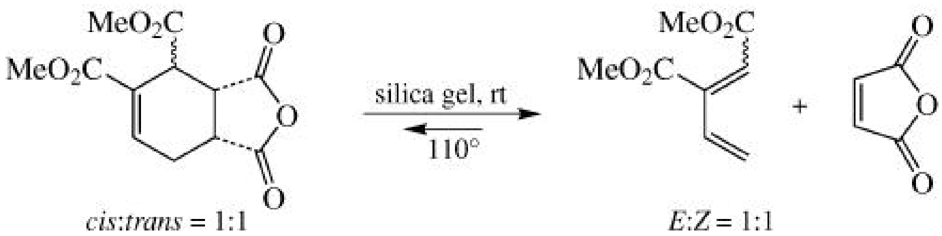
Only a few C-substituted maleimides have been synthesized by rDA methodology; one of the simple examples is illustrated. (465)



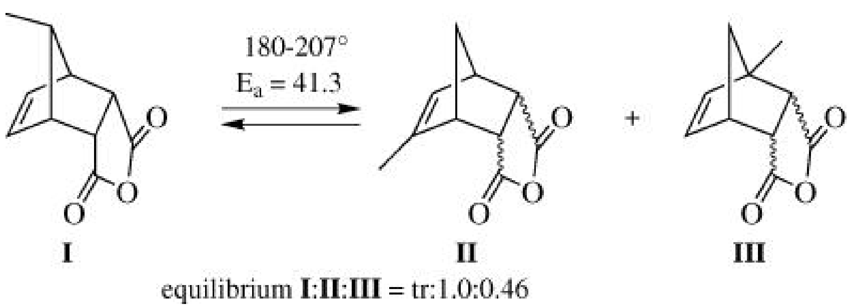
3.15.6. Maleic Anhydrides

MA has undoubtedly been the most widely utilized dienophile in DA reactions, and rDA reactions that (re)generate MA are numerous, as shown by the many entries in Table XI-F. Because of the long history of such reactions, many are found in early work in which yields (and conditions) were either not determined or cited.

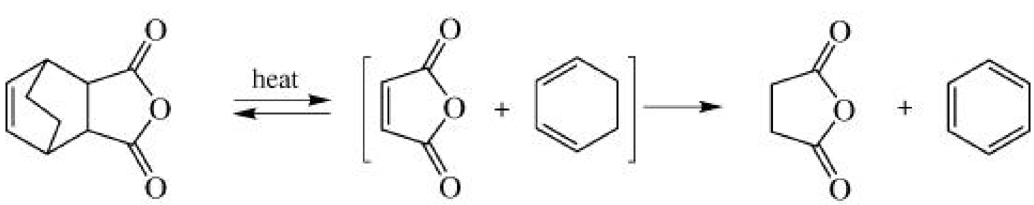
Only a few examples of formation of acyclic dienes formed by rDA expulsion of MA have been reported, presumably in part because of the high temperatures needed for such reactions (>300°). An exception is the formation of the *E,Z* isomers of 1,2-dimethoxycarbonyl-1,3-butadiene, which has been reported to occur at room temperature in a silica gel induced reaction. The implication is that the educt side of this equilibrium is favored at room temperature, perhaps because of stronger coordination with the silica gel, or decomposition of the MA. (184)



The MA-CP cycloadducts have been discussed in detail in the Mechanism section. One of the strong pieces of evidence favoring a dissociative mechanism comes from the study of the monomethyl derivative. The Me-CP diene that is generated undergoes facile [1,5]-H shifts, resulting in positional isomerization. Readdition of MA results in equilibration of the three isomers shown. (466) All three *endo* isomers interconvert to the same mixture of products under these conditions. (467)

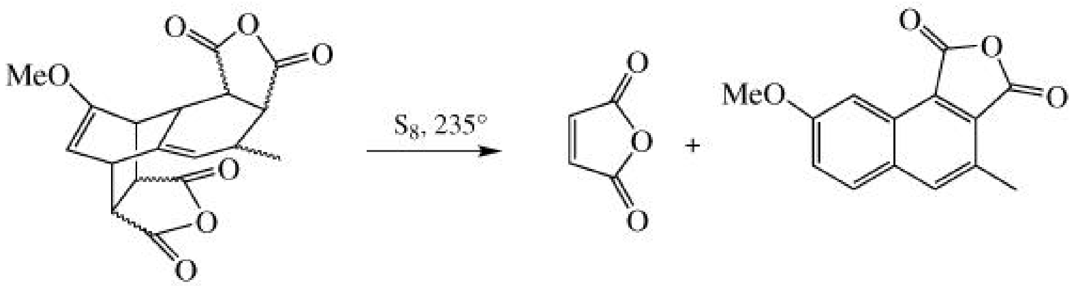


An early discovery made with the MA-cyclohexadiene adduct was that the educts, under the conditions needed for rDA reaction, undergo a subsequent redox reaction leading to the formation of succinic anhydride and benzene. (132)

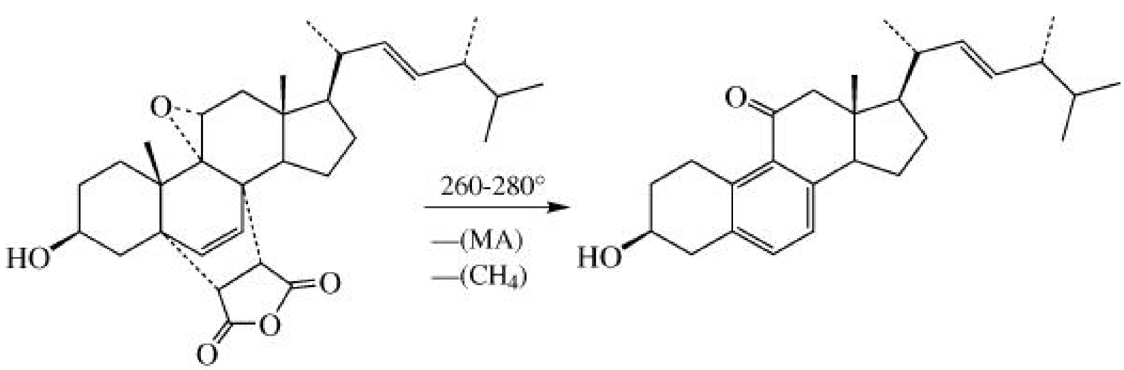


Similar redox reactions have also been observed in pyrolysis of MA-terpene cycloadducts. (468) The redox step can be circumvented by scavenging the MA as it is formed by an in situ diene; 1,4-diphenylbutadiene has been used for this purpose, allowing the isolation of substituted cyclohexadienes, with moderate success. (268)

Styrenes and 1,1-diarylethylenes react with excess MA to give bis-MA derivatives. When strongly heated under oxidative conditions, loss of one MA occurs along with aromatization, leading to naphthalene derivatives. In general the stereochemical details of the bis-adducts have not been determined. Many variants of this useful sequence are shown in Table XI-F. The products may be substituted naphthalenes that would be difficult to prepare by other methods. An example that illustrates this feature is shown. (469) In the absence of oxidant, simple rDA loss of MA occurs to regenerate the substituted styrene.

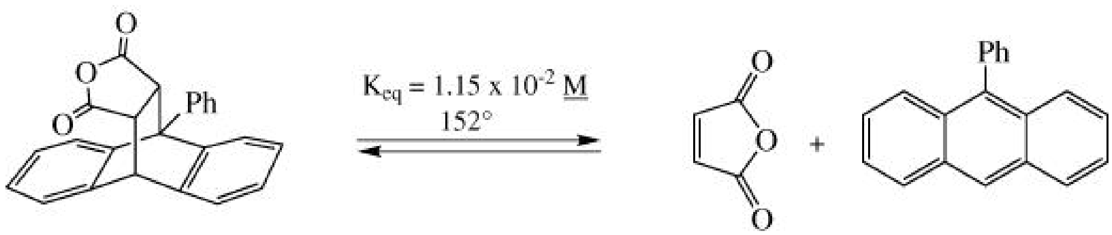


An unusual demethylation (loss of CH_4 ?) has been reported to accompany the rDA reaction of the MA-epoxydehydroergosterol adduct. (470)



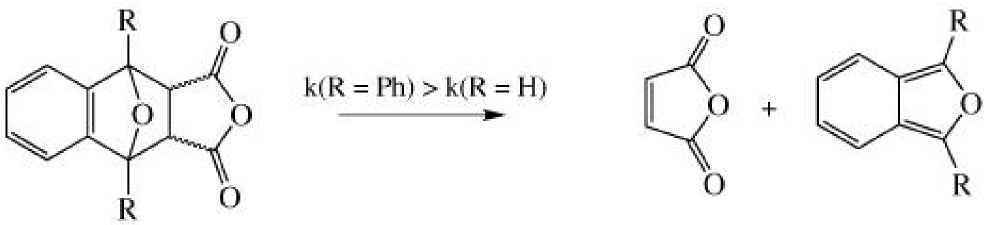
Naphthalene is a poor diene for DA reaction with MA, but (poly)methyl substitution appears to enhance both the rate and equilibrium position for cycloaddition, with reactions typically carried out in the 100–150° temperature range. It also appears that rDA rates are enhanced by such substitution, although care must be taken in interpretation of the mainly qualitative data in the literature. Several examples of substituted naphthalene adducts, and their rDA processes, are listed in Table XI-F; in most instances, the studies were carried out in the DA direction, and rDA features must be inferred.

Several qualitative observations on the effect of anthracene substituents on the DA/rDA equilibria with MA have appeared. These reactions typically require temperatures ³140°. While the relative amounts of educts/adduct are commonly listed in these equilibration studies, the concentrations are often not stated, preventing, with few exceptions, (471, 472) determination of a meaningful K_{eq}. In general it may be concluded that 9(10)-substitution diminishes the stability of adduct relative to educts, as illustrated for the 9-phenylanthracene system. (471)

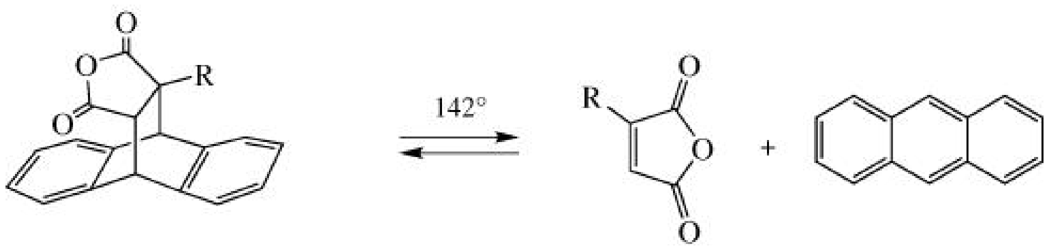


MA-furan adducts and some substituted analogs have been among the most carefully studied rDA substrates, as described in the Mechanism section. The parent MA-furan system remains the only example in which all four rate constants (formation/decomposition of *endo* and *exo* adducts) have been determined under identical conditions. (141) To the extent that one may generalize, it appears that substituents on the furan (2,5-dimethyl, (473) 3,4-dimethoxy, (474) 3,4-(bis)-trimethylsilyl (298)) enhance the rates of an already facile rDA process.

Isobenzofuran analogs behave similarly. The *endo* MA-1,3-diphenylisobenzofuran adduct (R = Ph) was reported in early work to dissociate at or slightly above room temperature, (475, 476) whereas the unsubstituted material (R = H) requires a temperature ³130° for convenient observation. (267)

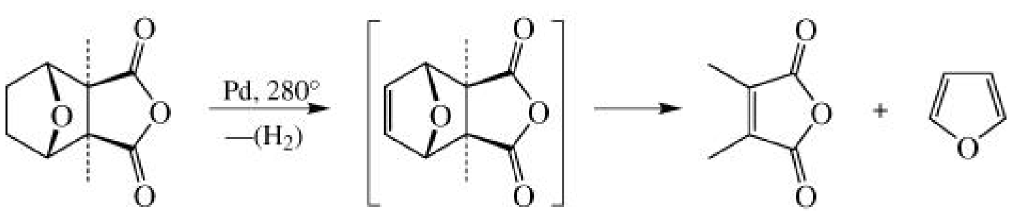


The rate and equilibrium constants for DA reaction of a series of substituted maleic anhydrides with anthracene have been reported. From these data, the rate and equilibrium constants (simple inverse) have been calculated, and these are displayed in Table XI-F. A few generalizations can be made. The change from R =H to R =alkyl (several examples) has a large effect (~400) on K_{eq}, but only modest differences in rates are observed. (477)



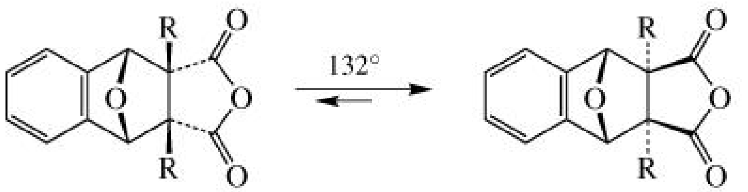
Similar effects on rate and equilibrium constants are found for substituted fumaric acid-anthracene adducts. (477)

In remarkable early work (1928), the reversibility of formation of the MA-furan adduct was recognized, and this knowledge was applied to structural work on cantharadin. Pyrolysis of the natural product in the presence of a (de)hydrogenation catalyst resulted in the formation of dimethylmaleic anhydride (and furan). (478)



cantharidin

The rate constants and K_{eq} values for interconversion of substituted MA-*endo* and *exo* isobenzofuran isomers have been determined. (267) The change from R = H to R = Me has a relatively small effect on K_{eq} (0.5 kcal/mol), and this effect is mainly associated with an increase in k_{exo} for the alkylated derivative, since k_{endo} is not greatly affected. (267) Note that only k_{exo} corresponds to a k_{rDA} in this example, and that knowledge of the kinetically controlled DA product ratio is needed to determine k_{rDA} for the *endo* isomer.

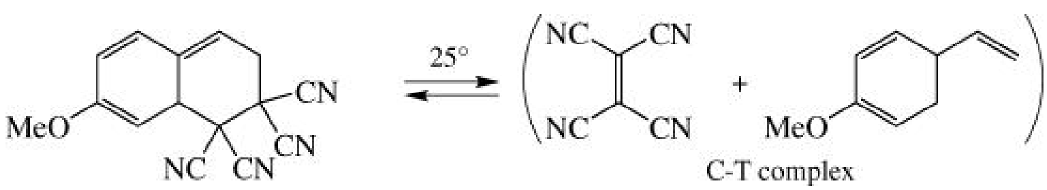


R	ΔG^0	k_{exo} x 10^{-6} s^{-1}
H	–2.4	5.9
Me	–1.9	150
Cl	—	190
$(CH_2)_4$	—	87

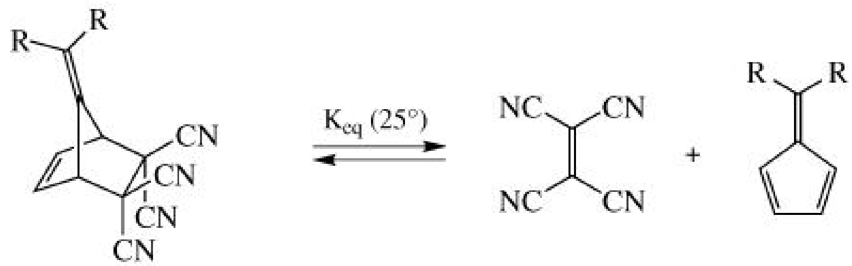
3.16. Tri- and Tetra-EWG-Substituted Alkenes

Only a handful of tri-EWG-substituted alkenes have been reported as products of rDA reactions, and no systematic study of these systems has been carried out. All the known examples are shown at the beginning of Table XII.

Of the three tetra-EWG-substituted dienophiles represented in Table XII, TCNE has been the most extensively studied. TCNE adducts of styrenes have been examined in some detail; rDA dissociation in several instances is thought to occur through a charge transfer complex intermediate, (479) as illustrated. Several other examples are listed in the table.

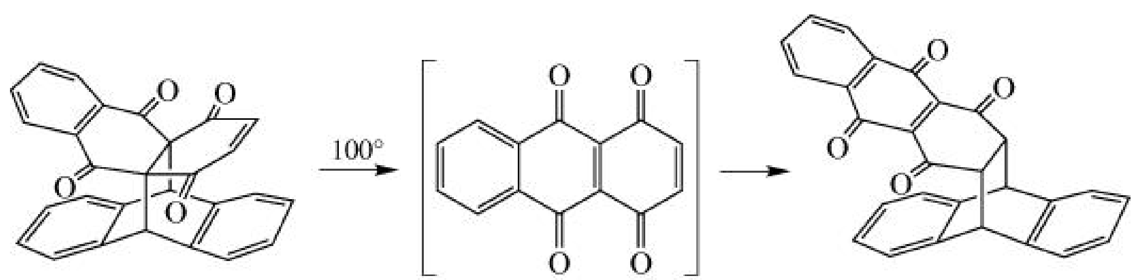


The exocyclic methylene substituents exert a strong effect on K_{eq} of TCNE-fulvene adducts, and several examples are found in Table XII. As one might expect, the more electron-withdrawing the substituents, the greater the tendency to dissociate (all examined at room temperature). The comparison between R = Ph(K_{eq} » 0.1) and R = *p*- $O_2NC_6H_4$(K_{eq} = 10) is noteworthy. (480)



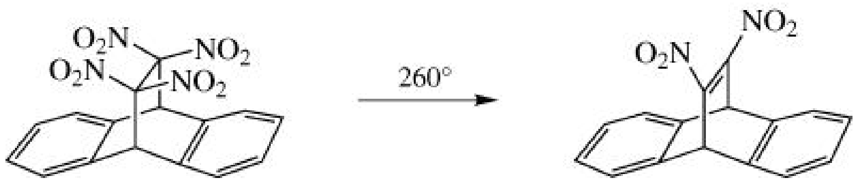
The TCNE-anthracene adduct also dissociates under relatively mild conditions (40–60°); the rate of this rDA reaction exhibits an appreciable solvent effect. (481) The corresponding 9-methoxyanthracene adduct dissociates at room temperature; TCNE has been scavenged from this reaction by the addition of 9,10-dimethylanthracene, giving the new adduct in excellent yield. (269)

A single example of a diquinone rDA reaction has been reported. Other DA reactions of this quinone gave products by reaction at the terminal dienophile site, but the novel anthracene adduct shown could be prepared at 25°. Upon heating, this adduct rearranges to the terminal dienophile adduct, presumably by an rDA/DA sequence. (482)



The third tetra-EWG-substituted alkene for which rDA information is available is the fascinating bis-anhydride analog of MA. This material resists direct preparation by classical anhydride forming reactions, and must be prepared after cycloadduct formation of a precursor; it is then generated as a reactive intermediate by rDA reaction. (269-273) Some of the unusual chemistry of this species has been discussed in the Scavengers section.

An effort to generate tetranitroethylene by rDA reaction of the anthracene adduct failed. Instead, the elements of N_2O_4 were lost to form the novel dinitroacetylene adduct. (483)



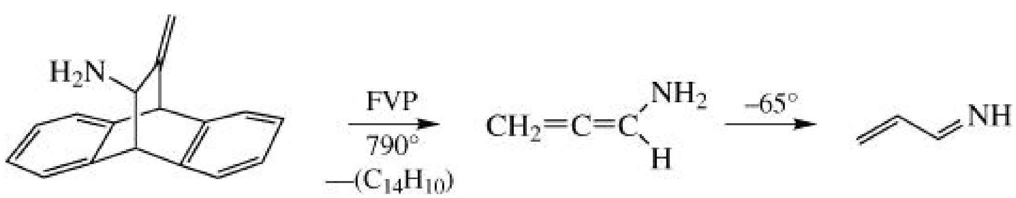
3.17. Heteroatom-Substituted Alkenes

This topic, and the corresponding sections of Table XIII, are divided by heteroatom substituent into three sections: alkenes substituted by nitrogen (one or more, with any additional substituent except an EWG); oxygen (and sulfur); and then miscellaneous heteroatoms. The formation of ketenes and related materials by rDA reactions is treated in the final section (Part I) of this review.

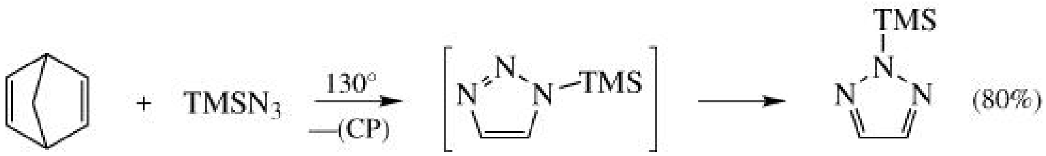
3.17.1. Nitrogen-Substituted Alkenes

The (resonance) stabilizing effects of heteroatom-bonded substituents on alkenes are well known. The transition state for a typical rDA reaction is expected to have products nearly fully formed, although otherwise held in adduct-like geometry. From this perspective, it is not surprising that heteroatom substituents can enhance the rates of rDA reactions, much like EWG groups. Quantitative effects are not easily predicted, but in fact enhancement is observed for most heteroatom substituents in the reaction of anthracene adducts. These effects range from negligible (OH, 1.3 relative to H), to moderate (NH_2, 83), to striking (NMe_2, 2500); interestingly, the ammonium substituent (NH_3^+) also leads to substantial rate enhancement (1700), presumably due to inductive stabilization of the transition state. The complete list of heteroatom substituents and k_{rel} values is given in Table XIII-A. (175)

Several enamines, including tautomerically unstable N - H compounds, have been prepared by rDA reactions, typically under FVP conditions with cold trapping of the products. An interesting example is the formation of allenylamine, which tautomerizes to acroleinimine at low temperature. (484, 485)

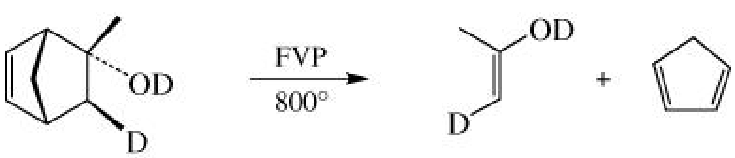


In addition to relatively simple enamines, the most commonly generated *N*-substituted dienophiles are five-membered aromatic heterocycles containing two or three N atoms, and oxazoles. Often the substrates for these reactions are formed by dipolar [3 + 2] reactions; an example is the trimethylsilyl azide addition to norbornadiene. (486)

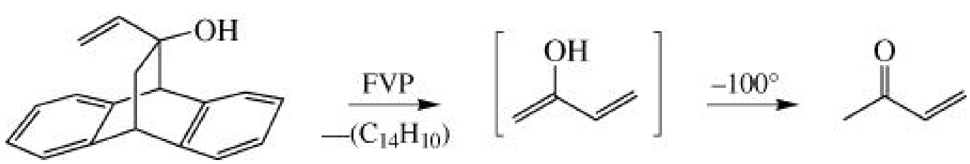


3.17.2. Oxygen-Substituted Alkenes

Hydroxy-substituted embedded dienophiles give enols, in characteristically stereospecific rDA reactions. FVP and cold trapping has proved to be a valuable approach to isolation of these metastable materials. The cycloadduct starting materials incorporate various dienes, with CP and anthracene the most commonly employed. One example, of many listed in Table XIII-B, is shown. (487)



Dienols are similarly accessible. The 1,3-butadien-2-ol isomer is especially difficult to isolate, with tautomerization to methyl vinyl ketone observed at low temperature. (485)

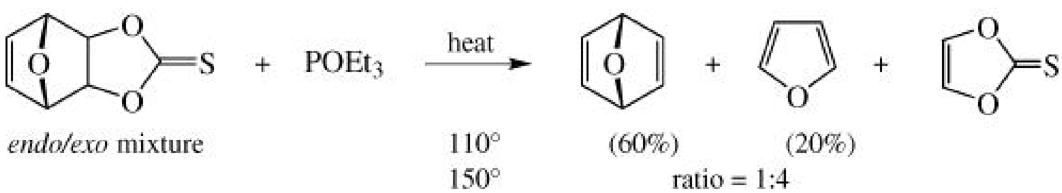


Oxyanionic species are much more reactive than the corresponding alcohols in rDA reactions. The formation of enolate ion from alkoxide is strongly favored thermodynamically by the relative acidities of alcohols (pK_a » 18) and enols

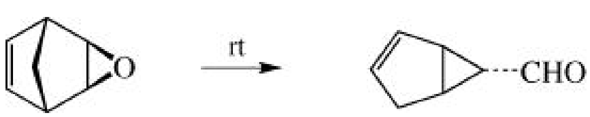
(pK_a » 10). This topic has been discussed in detail in the section on Base-Induced Reactions; several of the examples discussed there are found in Table XIII-B.

Acetate and other esters, and alkyl and trimethysilyl ethers have been successfully employed to prepare the corresponding vinyl derivatives by rDA reactions. Ketene acetals and ene-1,2-diols (simple or protected, e.g., as borate or other cyclic esters) have similarly been generated in straightforward rDA reactions.

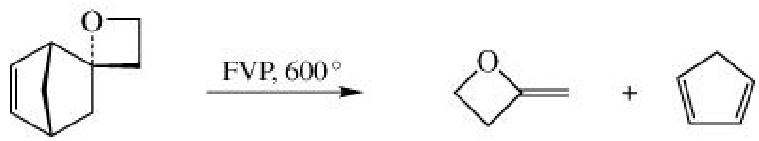
An intriguing report of the formation of 7-oxanorbornadiene, which is difficult to prepare by other means, utilizes desulfurization of the corresponding thionocarbonate. Variation of yield with temperature showed that this carbenoid reaction is in competition with rDA formation of vinylene thionocarbonate and furan, with the latter favored at higher temperature. (488)



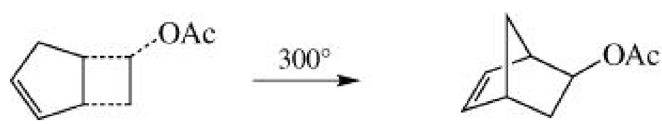
A portion of Table XIII-B is devoted to the several attempts, all unsuccessful, to prepare oxacyclopropene (acetylene oxide) by rDA methods. Since rDA methods have been used to generate and isolate many strained and unstable olefinic materials, it is perhaps not surprising that so much effort was expended in this search. A typical side reaction is rearrangement to an aldehydic isomer, or isolation of fragments from ill-defined processes. The norbornadiene monoepoxide is especially prone to (acid-catalyzed?) rearrangement. (489)



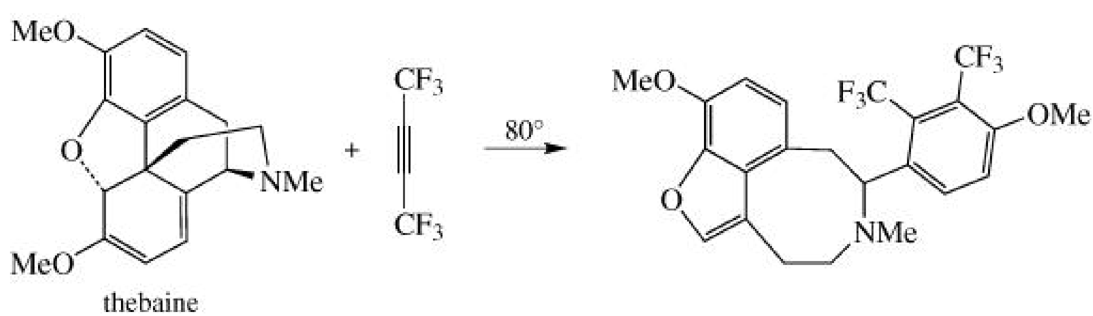
Other strained ethers have met with greater success. For example, FVP allows isolation of 2-methyleneoxacyclobutane in good yield, whereas simple gas phase pyrolysis causes further rearrangement of this product to methyl vinyl ketone. (490)



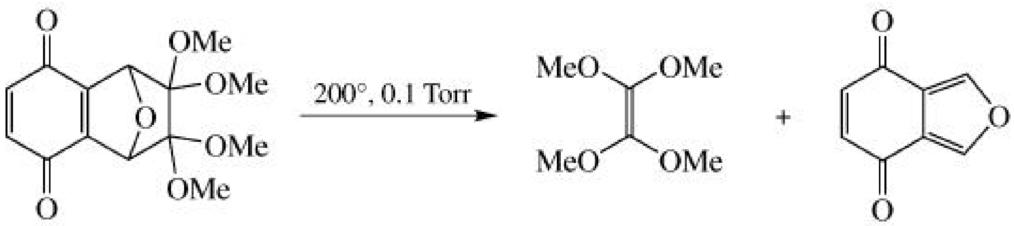
Occasionally rDA reactions interfere with mechanistic studies of other processes. For example, the stereochemistry of the rearrangement shown is complicated by interconversion of the *endo/exo* isomers of the product, presumably caused by rDA/DA reactions. (491)



DA reactions of thebaine with acetylenic dienophiles are often accompanied by Alder–Rickert type rDA reactions. The reaction with perfluoro-2-butyne illustrates this point. (492) Dienophile reactions with thebaine in general are subject to solvent effects, with DA reactions favored in benzene and Michael addition favored in acetonitrile. (493)



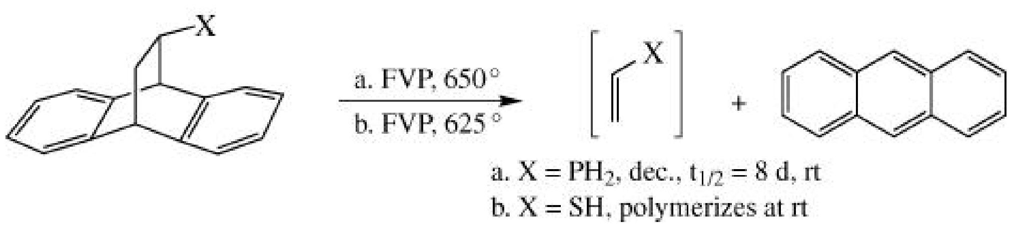
rDA expulsion of dienophiles bearing one or two oxygens are common. No examples with three oxygens are known. A single case of rDA expulsion of tetramethoxyethylene was found in a reaction leading to a novel furan-quinone. (494)



3.17.3. Other Heteroatom-Substituted Alkenes

Dienophiles bearing one or more of the following heteroatoms are collected in Table XIII-C, in order of increasing atomic number: B, F, Si, P, S, Cl, and Sn.

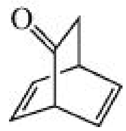
Interesting enol analogs include vinylthiol (polymerizes at room temperature), (495) and the relatively stable vinylphosphine (decomposes to unspecified products over several days). (496)



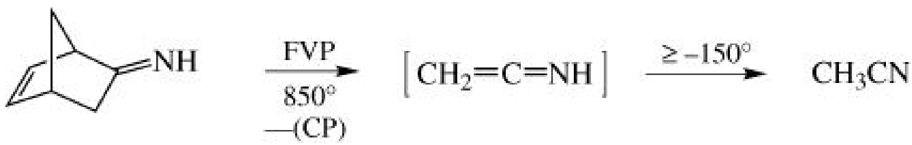
Some of the heteroatomic systems are represented, only or in addition to acyclics, by heterocyclic analogs of CP; these exhibit varying tendencies to undergo reversible DA dimerization.

3.18. Ketenes and Related Dienophiles

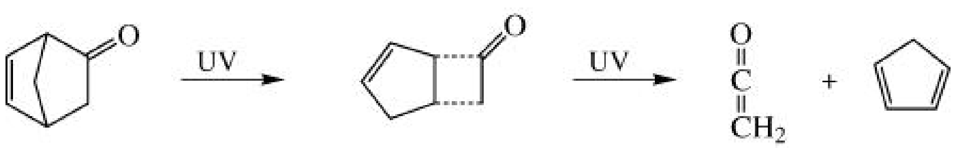
Although there are examples of thermal expulsion of ketenes and keteneimines in rDA reactions, inspection of the entries in Table XIV shows that most such reactions require unusually high temperatures, including those done under FVP conditions. Exceptions to this generalization involve uncommon substitution patterns. The mechanism of these thermal processes is unknown, but, whether stepwise or concerted, it is clear that thermal formation of ketene is not a favored process. A striking illustration is provided by the (formal) cycloadduct of ketene-benzene; it has been prepared at 180°, and purified by distillation without apparent decomposition. (497)



The parent keteneimine has been generated by high temperature FVP of the CP adduct. This interesting tautomer of acetonitrile rearranges to the nitrile at low temperature. (498)



The more general method of causing expulsion of ketenes from cycloadducts is UV irradiation. There is good evidence that these reactions occur as stepwise processes, involving initial Norrish I cleavage of the acyl-carbon bond. Rearrangement at this stage can lead to isolable intermediates. For example, UV treatment of the bicyclo[2.2.1] ketone affords the bicyclo[3.2.0] ketone. Further irradiation effects retro[2 + 2] reaction. The final products are thus ketene and CP, the products expected of formal rDA reaction. (499)



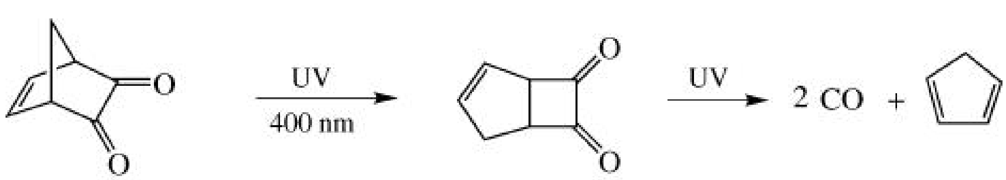
Analogous UV-induced rearrangements of substituted bicyclo[2.2.2] ketones to bicyclo[4.2.0] systems occur under conditions where subsequent retro[2 + 2] reaction is suppressed. (500)

Norrish I initiated intramolecular rearrangement, with trapping by solvent methanol, is evident in the reaction. Minor amounts of 9-methylanthracene, expected from rDA reaction, accompany the product. (501)

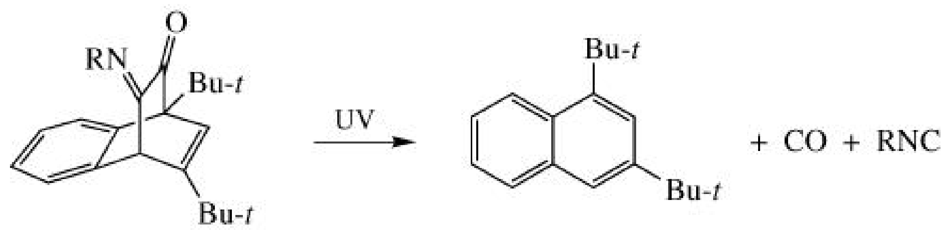
Formal cycloadducts of (O =C = C =O) have been extensively studied by rDA methods in efforts to generate this unknown species. Calculations indicate that C_2O_2 is unstable relative to 2 CO, (502) and CO is indeed formed in these reactions, although the mechanistic details are unknown. The dione cycloadducts have typically been prepared by sequences that utilize DA reactions of a dihalovinylene carbonate (a masked form of C_2O_2) followed by hydrolysis. (503)

The (formal) benzene adduct appears to be at least moderately stable. It has been isolated and found to behave normally (double bond reduction) under catalytic hydrogenation conditions, (504) but the limits of its thermal stability have apparently not been tested. A bis-imine anthracene adduct analog has also been described, and is reported to undergo “little or no” rDA reaction when heated, or interestingly, when UV irradiated. (505)

Other similarities exist between the 1,2-dione adducts and those of ketene. For example, the bicyclo[2.2.1] dione rearranges under relatively low energy UV treatment to the isolable bicyclo[3.2.0] dione; further irradiation leads to the formation of CO and CP. (506)



UV irradiation of a 1,2-dione monoimine (R = Pr,Ph, C_6H_{13},OH) is reported to generate the isonitrile in good yield, along with the substituted naphthalene and CO. (507, 508)



Thioketene and dimethylthioketene have been formed by FVP rDA reactions of the CP and anthracene adducts, (331, 509) in processes that are similar to those for the corresponding ketene analogs

4. Experimental Conditions

Although there is fundamentally only one variable— internal energy— that can affect the rDA or any other kinetically first-order process, and there are only a few distinct ways of introducing this energy (heat, UV), the range of substrates and temperatures (–200° to 1000°) associated with rDA reactions is such that there is no “typical” condition that can be cited. Heating can take place in open flasks, sealed tubes, or flow systems, in the solid, liquid, or gas phase. Suitably substituted cycloadducts are susceptible to acid catalysis, or induction by acids or bases, as discussed in detail in earlier sections.

Readily reversible DA/rDA paired reactions can be controlled simply by change of concentration, taking advantage of the fact that the K_{eq} for a first-order/second-order equilibrium is concentration dependent. Or, the rDA reactions can be driven to completion by removal of either diene or dienophile. For volatile materials, this is often best accomplished by evaporation. For less volatile materials, the use of an in situ scavenger, as discussed in the section on this topic, can be effective.

The flash vacuum pyrolysis (FVP) method has advantages in many applications. The advantages derive from short hot zone contact times and rapid cooling of effluent that often has allowed the isolation of very reactive or metastable species. Several good reviews of this technique and descriptions of experimental apparatus have appeared. (14-23)

5. Organization of Tables

Tabulation of the data with strict adherence to normal Organic Reactions rules would not result in a very useful format for the reader. Since the rDA reaction typically leads to two products (dienophile and diene) without uniformity as to which is the more significant, it was decided arbitrarily to separate tables according to dienophile, starting with " C_2H_2 and other Acetylenes". Since the number of entries for this topic is relatively small, all reactions leading to expelled acetylenic dienophiles are included in Table I. Table II lists the many reactions that generate ethylene, followed by several tables for different types of substituted ethylenes. These are prioritized as follows: alkyl (mono-, di-, tri- and tetra-, in three tables), vinyl- and aryl-substituted olefins, and a short table on allenic dienophiles. Reactions that expel aromatic dienophiles warrant a separate table, with carbocyclics followed by heteroaromatic dienophiles. These are followed by tables of electron-withdrawing-group (EWG) substituted olefins, with separate listing for mono-EWG alkenes (large number of entries), di- (very large), and tri- and tetra-EWG olefins as the expelled dienophiles. Heteroatom-substituted (arranged in order of atomic number) alkenes are treated next, followed by a table on ketenes to complete Part I of this review. Expelled dienophiles in which one or both of the reaction centers is a heteroatom are found in Part II of this review.

To avoid duplication of entries for alkenes bearing two or more different kinds of substituents, prioritization was made on the basis:
EWG > heteroatom > vinyl/aryl > alkyl; thus, expulsion of a dienophile with all of these substituents would be found in the mono-EWG alkene table.

Organization within each table differs from the usual Organic Reactions format in that no effort is made to prioritize according to carbon count of the starting material (typically a cycloadduct but in many instances a mixture of adduct precursors). Instead, it was recognized that further organization *within* each table by the structural type of dienophile (e.g. open chain, increasing ring size) and by the type of diene expelled, would be a valuable feature for accessing specific examples and making comparisons among related reactions. Within each table, the "dienes" are prioritized as butadiene, substituted butadienes (with substituents as above), cyclopentadienes, cyclohexadienes, etc., aromatics, 6-membered heteroaromatics, 5-membered heterocycles, etc.

Several of the reactions described involve an initial DA reaction followed by a (different or exact reverse) rDA. In most instances, the initial reagents are tabulated as "Starting Material", with the cycloadduct inferred or occasionally depicted. No separate "Reagents" column is used, since this is rarely pertinent to rDA reactions. Added reagents are either shown as "Starting Materials" or under “Conditions”.

All energies are stated in kcal/mol, with entropy terms in cal/mol.deg, and these units are omitted unless needed for clarity in the text. In keeping with Organic Reactions norms, all temperatures are given in °Celsius, including very high temperatures that would more typically be found in K.

The following abbreviations are used in the tables.

$C_{14}H_{10}$	anthracene
CP	cyclopentadiene
Cp	cyclopentadienyl anion
DMAD	dimethyl acetylenedicarboxylate
LDA	lithium diisopropylamide
LTMP	lithium tetramethylpiperidide
MA	maleic anhydride
MTAD	*N*-methyltriazolinedione
NMM	*N*-methylmaleimide
NPM	*N*-phenylmaleimide
PTAD	*N*-phenyltriazolinedione

Table I. Acetylenic Dienophiles

View PDF

Table II. Ethylene

View PDF

Table III. Monoalkylethylenes

View PDF

Table IV. 1,1-Dialkylethylenes

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Table V. 1,2-Dialkylethylenes

View PDF

Table VI. Tri- and Tetraalkylethylenes

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Table VII. Aryl- and Vikyl-Substituted Olefins

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Table VIII. Allenes and Related Polyenes

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Table IX. Aromatic and Heteroaromatic Compounds

View PDF

Table X. Mono-EWG Substituted Alkenes

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Table XI-A. 1,1-Di-EWG Substituted Alkenes

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Table XI-B. Acyclic 1,2-Di-EWG Substituted Alkenes

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Table XI-C. Cyclic 1,2-Di-EWG Substituted Alkenes

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Table XI-D. Quinones as Dienophile

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Table XI-E. Maleimides

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Table XI-F. Maleic Anhydride

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Table XII. Tri- & Tetra-EWG Alkenes

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Table XIII-A. Nitrogen-Substituted Alkenes

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Table XIII-B. *O*-Substituted Alkenes

View PDF

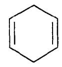
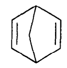
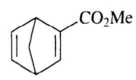
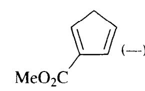
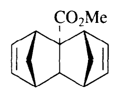
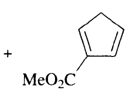
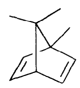
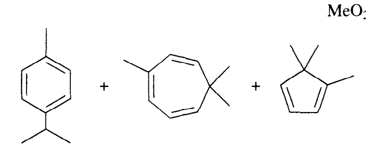
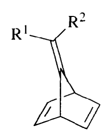
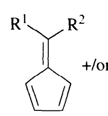
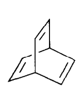
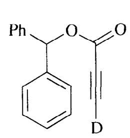
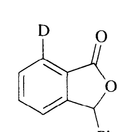
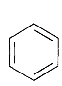
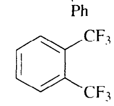
Table XIII-C. Other Heteroatom-Substituted Alkenes

View PDF

Table XIV. Ketenes and Related Alkenes

View PDF

TABLE I. ACETYLENIC DIENOPHILES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Pulsed laser, SF_6	C_2H_2 + butadiene (both minor) + benzene (>95) + H_2	295
	327 - 357°, $E_a = 50.5$, $A = 5.2 \times 10^{14}$	C_2H_2 + CP (—)	510
	320 - 360°, $E_a = 49.8$, $\Delta S^{\ddagger} = -2.5$	C_2H_2 + CP (—) + toluene (minor)	294
	344 - 431°, $E_a = 50.5$, $A = 5.2 \times 10^{14}$	C_2H_2 + CP (—)	511
	252 - 383°	C_2H_2 + CP (—) + toluene (minor) + 1,3-cycloheptadiene (—)	512
	Pulsed laser, SiF_4	C_2H_2 + CP (—)	513
	Pulsed laser, SF_6	C_2H_2 + CP (—) + toluene (—)	514
	γ-Radiolysis	C_2H_2 + $[CP]^{+\cdot}$ (—)	515
	n-Amyl Na	C_2H_2 + Na-Cp	242
	FVP, 870°	C_2H_2 + CP + ≡—CO_2Me +  (—)	516
	FVP, 870°	C_2H_2 + CP + ≡—CO_2Me (20) +  (25)	516
	272°	 ratio: 0.3 : 1.0 : trace	517
	FVP	C_2H_2 +  **I** +/or C_6H_6 + **II** $[R^1R^2C:]$	518
	210 - 250°, $E_a = 41.7$ kcal/mol, log A = 14.27	C_2H_2 + benzene (—)	282
	250°	C_2H_2 + benzene (—)	519
	640°	C_2H_4 +  (—)	520
 + F_3C—≡—CF_3	≥ 180°	(C_2H_2) +  (minor)	521

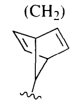
R^1	R^2	Temp	I (%)	II (%)
H	H	300°	96	tr
D	D	300°	no CD_2	
Me	Me	300°	80	—
F	F	300°	30	—
$S(CH_2)_3S$		350°	78	—
Br	Br	300°	67	—
H	OMe	600°	63	—
H	Ph	500°	78	—
H	$CH{=}CH_2$	500°	—	—
CN	CN	450°	—	—
$(CH_2)_4$		500°	—	—
TMS	TMS	400°	0	100
$(CH_2)_2$		400°	0	67
(CH_2)		400°	0	16
		400°	0	72

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

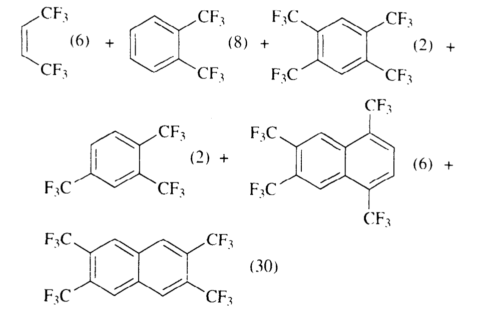
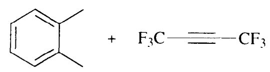
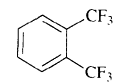
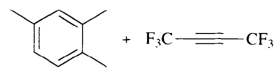
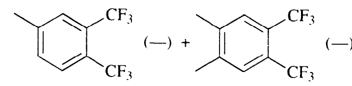
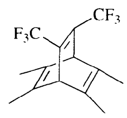
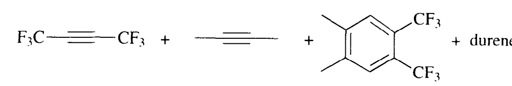
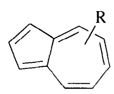
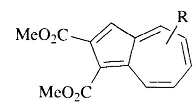
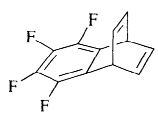
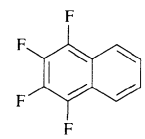
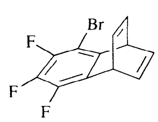
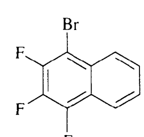
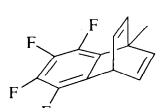
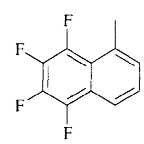
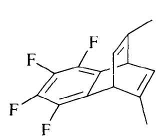
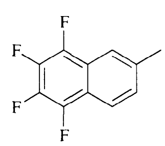
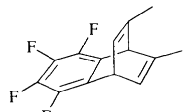
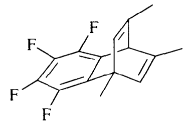
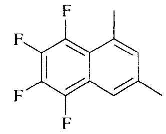
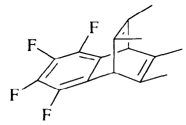
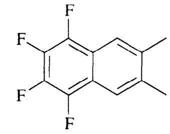
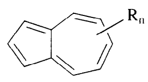
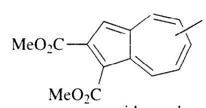
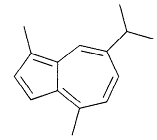
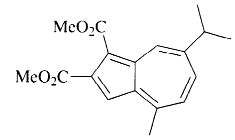
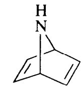
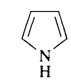
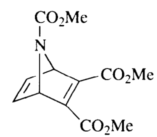
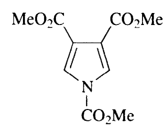
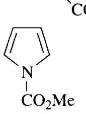
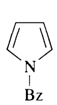
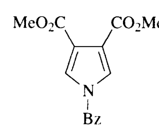
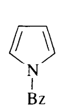
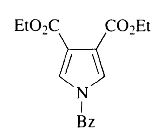
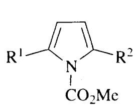
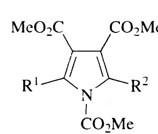
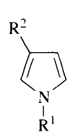
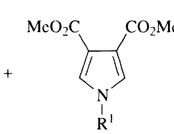
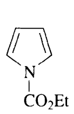
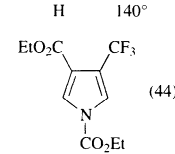
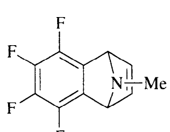
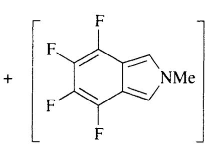
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	250°		522, 523
	200°	(2-butyne) +  (minor)	521
	220°		521
	250°		522, 523
 + DMAD R = alkyl	$RuH_2(Ph)_4$	(C_2H_2) + 	524
	330°	C_2H_2 +  (87)	525
	350°	C_2H_2 +  (85)	525
	350°	C_2H_2 +  (61)	525
	350°	 **I** +  **II** (70)	525
	350°	**I** + **II** (70)	525
	400°	**I** +  (75)	525
	400°	+  (70)	525

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD R = H, Me, alkyl, OMe, CO_2Et	207°	C_2H_2 +  (0-56) side product in heptalene synthesis	526
	Rh or Ru catalysts	rDA side product diminished	224
 + DMAD	208°	C_2H_4 + +  (6)	527
	≥ 80, $t_{1/2}$ (100°) = 7.5 h	C_2H_2 +  (—)	296
	170°	C_2H_2 +  **I** (—)	528
 + DMAD	200°, 1 h	C_2H_2 + **I** (40)	529
	190°, 2.5 h	C_2H_2 + **I** (35)	530
 + DMAD	190°, 2.5 h	C_2H_2 +  (67)	530
 + EtO_2C—≡—CO_2Et	190°, 2.5 h	C_2H_2 +  (54)	530
 + DMAD	160°, 1 h	C_2H_2 +  R^1 / R^2: H / H; Me / Me; H / Me; Ph / Ph no reaction	531
 + DMAD	heat	≡—R^2 + 	532
 + EtO_2C—≡—CF_3	140°	C_2H_2 +  (44)	533
	325°	C_2H_2 +  (≥ 27)	534

Ref. 532 products:

R^1	R^2	Temp	Yield (%)
Me	Me	rt, exoth.	(3)
t-Bu	H	115°	(2)
Ph	H	140°	(48)
p-$MeOC_6H_4$	H	140°	(7)
p-BrC_6H_4	H	140°	(19)
p-$O_2NC_6H_4$	H	140°	(12)
Ac	H	140°	(12)

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

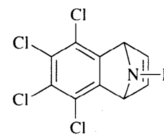
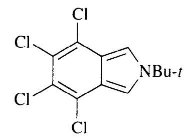
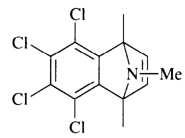
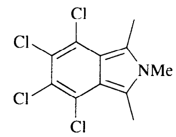
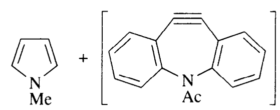
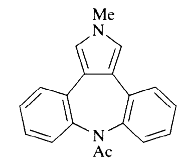
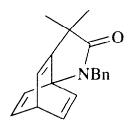
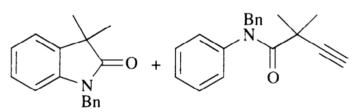
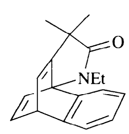
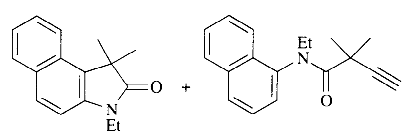
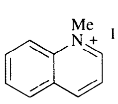
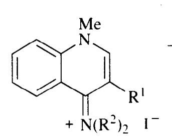
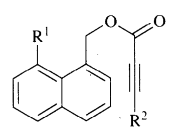
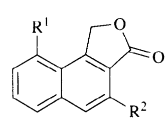
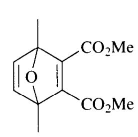
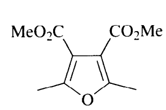
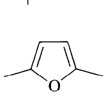
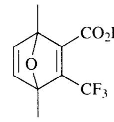
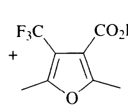
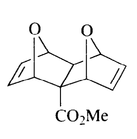
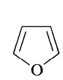
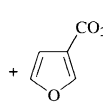
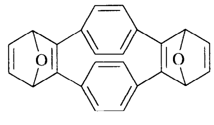
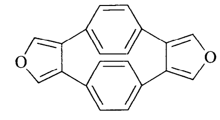
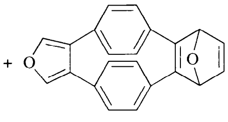
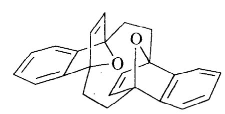
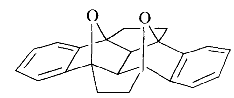
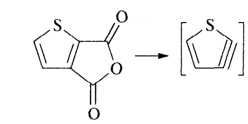
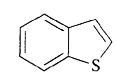
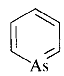
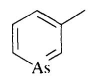
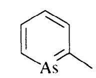
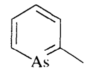
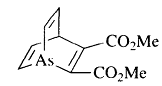
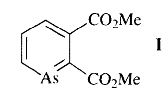
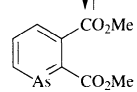
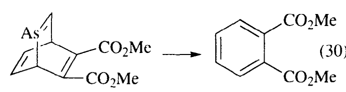
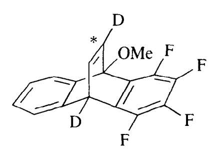
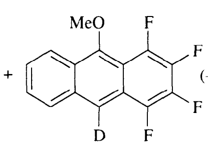
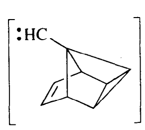
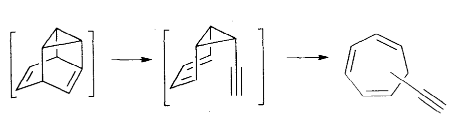
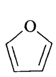
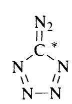
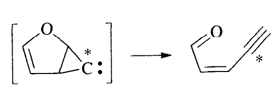
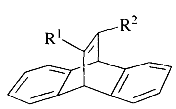
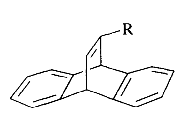
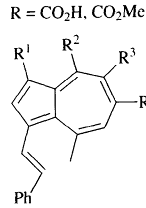
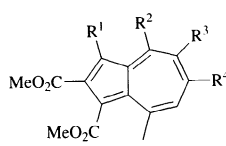
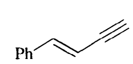
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	220°	C_2H_2 +  **I** (27)	535
	≥ 200°	C_2H_2 + **I** (—)	536
	≥ 200°	C_2H_2 +  (—)	536
	112°	C_2H_2 +  (31)	537
	150°	 **I** (—) (—) + C_2H_2	223
	$Co_2(CO)_8$, 80°	C_2H_2 + **I** (—)	223
	150°	 + C_2H_2 **I** (—) (—)	223
	$Co_2(CO)_8$, 80°	C_2H_2 + **I** (—)	223
 + $R^1—≡—N(R^2)_2$	rt	 R^1 R^2 Yield (%) Ph Me (45) Ph Et (50) *t*-Bu Me (75) + C_2H_2	538
	FVP, 750°	 R^1 R^2 Yield (%) H H (73) Ph H (70) H Ph (68) + C_2H_2	539
	180-210°	C_2H_2 +  (65)	540
 + $EtO_2C—≡—CF_3$	120-160°	 (10) +  (90) + C_2H_2	533
	500°, 10^{-6} Torr	C_2H_2 + $EtO_2C—≡$ (30) +  +  (50)	516
	FVP, 240°	C_2H_2 +  **I** (60)	541
	FVP, 240°, short contact time	C_2H_2 + **I** (34) +  (27)	541

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

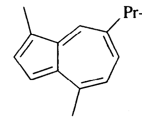
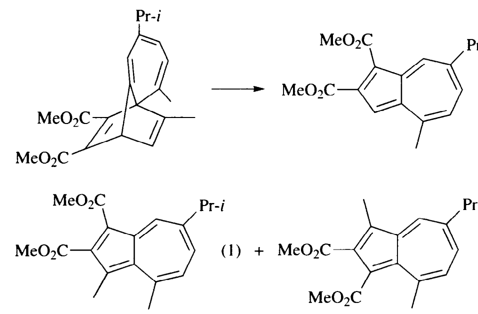
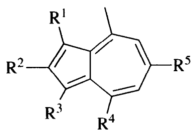
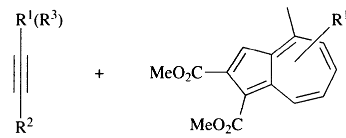
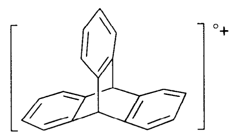
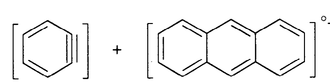
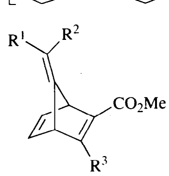
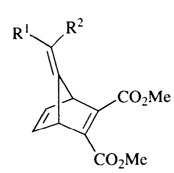
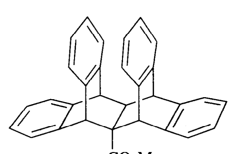
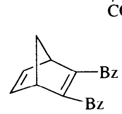
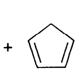
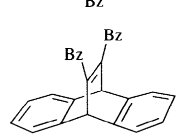
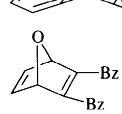
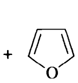
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	150°, 4 h	C_2H_2 +  (27)	542
 + C_6H_6	FVP, 500°	C_2H_2 +  (17)	543
 + ≡—CO_2Me	1. 100° (bicyclics) 2. 400°	 +  (—) 3:2	544
 + DMAD	Heat	Four products, consistent with (—) mechanism shown above	544
 ⇅ 80°	400°, GLC	C_2H_2 +  **I** (80)	544
 + DMAD	210°	 (30) + **I** (32)	544
	FVP, 600°	≡*—D (~40) +  (—)	545
 generated photochemically	−78°	 (1)	546
 + 	—	 (—)	547
	FVP, 500-550°	R^1—≡—R^2 + $C_{14}H_{10}$	299

R^1	R^2	Yield (%)
H	Ph	(~100)
Me	Ph	(~100)
Et	Ph	(~100)
Bn	Ph	(~100)
Me	Et	(82)
Et	Et	(80)
Bn	Me	(60)
Bn	Et	(72)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = CO_2H, CO_2Me, CH_2OH	FVP, 800-850°	≡—R (50-60) + $C_{14}H_{10}$	300
 + DMAD	190-200°	 + 	548

R^1	R^2	R^3	R^4	
H	Me	H	Me	(44)
Me	H	*i*-Pr	H	(20)

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	208° (⇌)	 (5); (1) + (12)	549
 + DMAD	180 - 200°	 I	550
	$AlCl_3$	 (—)	302
 + DMAD R^1, R^2 = Ph,Ph; H,Ph; Me,Me R_3 = H or Ph	Heat	R^3—≡—CO_2Me +  (—)	551
	890°, 10^{-6} Torr	≡—CO_2Me (20) + $C_{14}H_{10}$	516
	160°, 4 h	Bz—≡—Bz I +  (63)	297
	260°, 2 h	I + $C_{14}H_{10}$ (83)	297
	100°, 4 h	I (91) + 	297

R^1	R^2	R^3	R^4	R^5	
Me	H	Me	Me	Me	(~1)
Me	Me	Me	Me	Me	(<0.5))
Me	H	Me	Me	*n*-Pr	(40)
Me	H	Me	Me	*t*-Bu	(—)
Me	H	H	Me	Me	(39)
Me	Me	H	Me	Me	(10)
Me	H	H	Me	*t*-Bu	(18)
Me	H	Me	H	Me	(21)
H	Me	H	Me	Me	(7)
H	CO_2Me	H	Me	Me	(26)

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

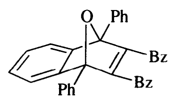
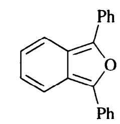
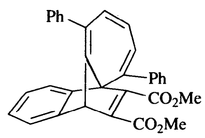
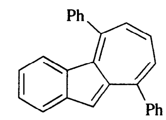
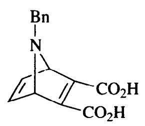
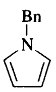
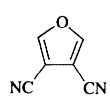
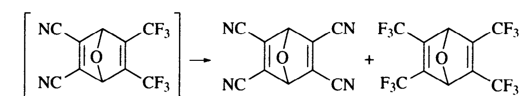
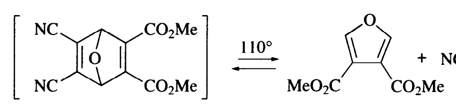
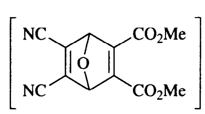
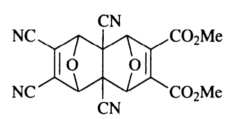
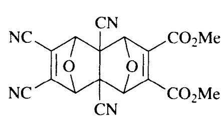
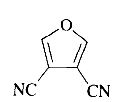
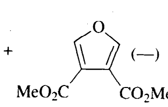
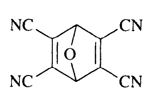
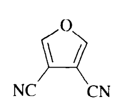
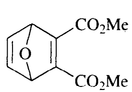
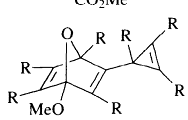
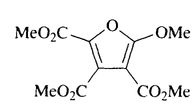
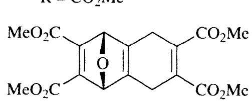
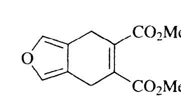
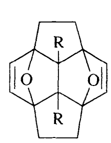
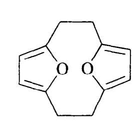
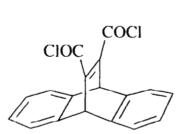
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	210°, 12 h	I +  (44)	297
	150°, DMF	 (15) + DMAD	552
	10% aq.Na_2CO_3, reflux 12 h	 (—) + NaO_2C—≡—CO_2Na	239, 240
 + F_3C—≡—CF_3 I	160°	 (35) (30)	553
I + DMAD	110°	 + NC—≡—CN	554
 + I	110°	 (—)	554
	218°	 +  (—) + NC—≡—CN	554
	EtOH, HCl, 80°	 + NC—≡—CN (—)	554
	TFA or RCO_2H	 + DMAD (—)	540
 thermal tetramer of DMAD R = CO_2Me	100 - 180°	 (low) + DMAD (low)	555, 556
	heat	 (100) + DMAD	557
	pyrolysis	 (—) + DMAD	558
 + MA (4 equiv) R = CO_2Me	185 - 195°, 2.5 h	ClOC—≡—COCl (—) + $H_{10}C_{14}$—MA	261, 262

TABLE I. ACETYLENIC DIENOPHILES (*Continued*)

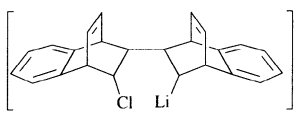
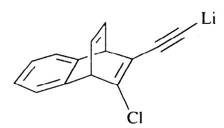
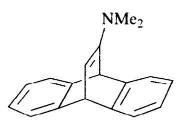
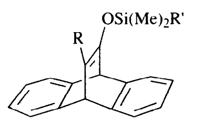
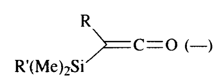
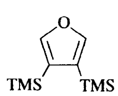
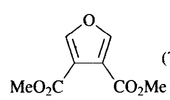
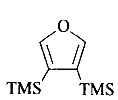
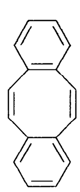
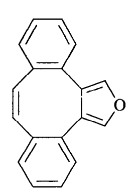
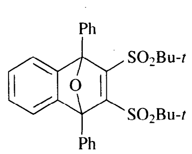
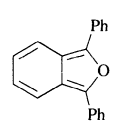
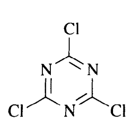
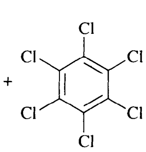
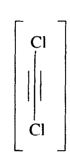
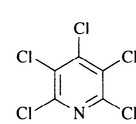
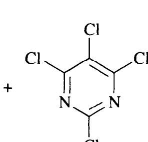
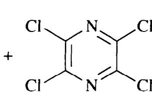
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	65°	 + $C_{10}H_8$	249
	FVP, 650°	≡—NMe_2 (80) + $H_2C=C=NMe$ (20) + $C_{14}H_{10}$	300
	FVP	 (—) + $C_{14}H_{10}$	300
 + DMAD	70°	 (73) + TMS—≡—TMS (1)	298
 + 	rt	 (3) + TMS—≡—TMS (—)	298
	112°, few min ⇄ 5°	 + t-BuO_2S—≡—SO_2Bu-t	559
 + 	K_{eq} ca. 2, 600°	 ⇄  +  + 	560

TABLE II. ETHYLENE

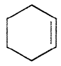
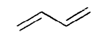
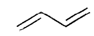
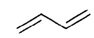
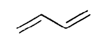
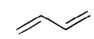
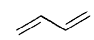
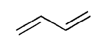
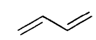
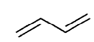
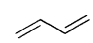
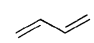
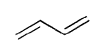
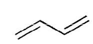
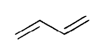
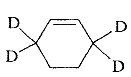
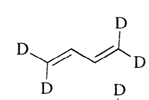
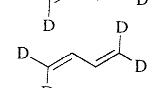
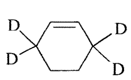
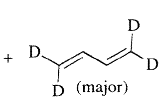
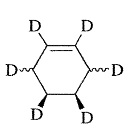
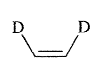
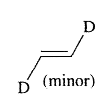
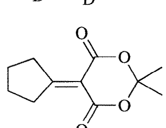
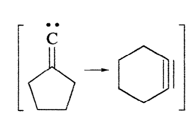
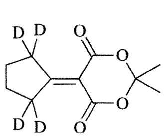
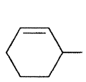
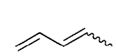
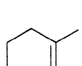
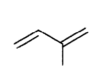
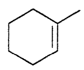
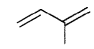
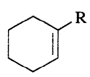
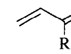
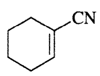
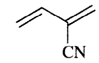
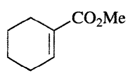
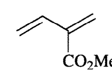
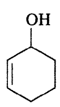
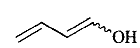
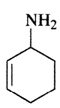
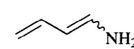
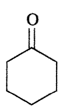
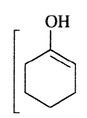
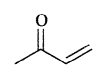
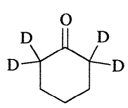
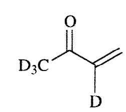
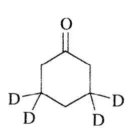
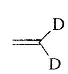
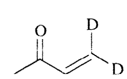
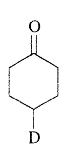
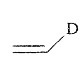
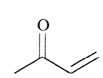
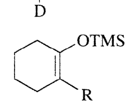
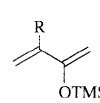
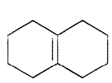
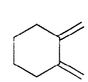
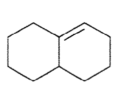
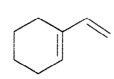
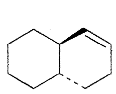
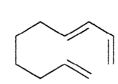
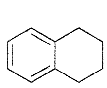
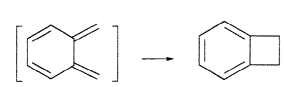
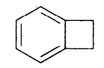
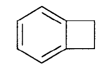
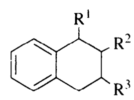
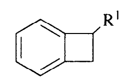
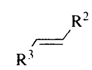
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	650°	C_2H_4 (78) +  (65)	561
	vapor, glowing Pt wire	C_2H_4 (—) +  (—)	562
	700 - 800°, flow pyrol.	C_2H_4 (—) +  (90)	563
	485 - 565°; E_a = 57.5 $\Delta S^{\#} = -1.4$	C_2H_4 (—) +  (—)	564
	665 - 745°; $\Delta H^{\#} = 55.1$ $\Delta S^{\#} = -5.5$	C_2H_4 (—) +  (—)	565
	425 - 535° $k = 1.4 \times 10^{17} e^{(-72,700/RT)}\ s^{-1}$	C_2H_4 (—) +  (—)	566
	541 - 629°, 25 Torr E_a = 66; log A = 15.2	C_2H_4 (—) +  (—)	307
	627 - 877°, shaker tube E_a = 66.7; log A = 15.0	C_2H_4 (—) +  (—)	333
	677 - 827°, shaker tube	C_2H_4 (—) +  (—)	567
	pulsed laser, SiF_4	C_2H_4 (—) +  (—)	513
	heat, shaker tube or static BCl_3 (no catal.)	C_2H_4 (—) +  (—)	183
	927 -1727°; E_a = 65.7 log A = 15.6	C_2H_4 (—) +  (—)	568, 569
	UV 193 nm, or pulsed IR laser	C_2H_4 (—) +  (—)	570
	UV	C_2H_4 (—) +  (—)	571
	477 - 525°	C_2H_4 (—) +  (—)	572
	UV, 185 nm	C_2H_4 (—) traces D +  (—)	303
	UV, 105 nm	$C_2(H{+}D)_4$ (—) + $C_4(H{+}D)_6$ (—) extensive H.D scrambling	303
	804 - 922°	C_2H_4 (major) + $H_2C{=}CD_2$ (minor) +  (major)	304
	821 - 971°	 (90) +  (minor) + $C_4H_2D_4$ (not anal.)	304
	450 - 650°	 → C_2H_4 + $H_2C{=}C{=}C{=}CH_2$ (—)	573
	450 - 650°	C_2H_4 + $D_2C{=}C{=}C{=}CD_2$	573
	UV, Hg ($^3P_1$) sensit.	H_2 + CH_4 + C_2H_4 +  (—)	574
	690°	C_2H_4 (75) +  (35)	561

TABLE II. ETHYLENE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	727 - 907°; E_a = 69.3	C_2H_4 (—) +  (—)	575
	710 - 750°	C_2H_4 (—) +  I; R, I (%), II (%), CH_4: Me, —, 80, —; Et, 52, —, 35; Ph, 87, 41, —	576
	FVP, 630°, 23% conversion	C_2H_4 (98) +  (71)	577
	FVP, 750 - 850°	C_2H_4 (—) +  (—)	578
	FVP, 900°	C_2H_4 (—) +  (—) *E* (major)	330
	FVP, 900°	C_2H_4 (—) +  (—)	330
	FVP, 1050°	 → C_2H_4 (85) +  (25)	305
	FVP, 1050°	C_2H_4 (—) +  (—)	305
	FVP, 1050°	 not isolated +  (—)	305
	FVP, 1050°	 not isolated +  (no D) (—)	305
 R = H, Me, or *n*-Pr	900°	C_2H_4 (—) +  (10 - 60)	579
	flow, 600 - 725°; E_a = 62.2°	C_2H_4 (—) +  (—)	308
	flow, 600 - 725°; E_a = 57.2°	C_2H_4 (—) +  (—)	308
	flow, 600 - 725°; E_a = 65.2°	 (—)	308
	energy source	C_2H_4 (—) +  I	580, 311

energy source	I (%)
N_2 flow pyrolysis, 750°	2
FVP, 750°	35
Laser IR pulse irrad.	55 - 73
SiF_4, IR pulse (1490°)	38

TABLE II. ETHYLENE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	pulsed laser, SiF_4	C_2H_4 (—) +  (—)	581
	1000 - 1400°, shaker tube $k = 3.5 \times 10^{15}\, e^{(-40{,}000/T)}\, s^{-1}$	C_2H_4 (—) +  (—)	306
	gas phase, heat	 I +  (—)	582

R^1	R^2	R^3	Temp	I (%)
H	H	H	737°	6
Me	H	H	732°	0
H	Me	H	797°	7
H	Me	Me	737°	8
H	*cis*-$(CH_2)_4$	*cis*-$(CH_2)_4$	758°	24
H	*trans*-$(CH_2)_4$	*trans*-$(CH_2)_4$	752°	tr

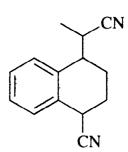
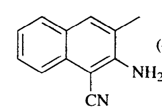
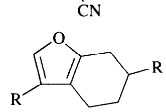
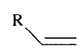
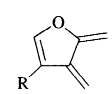
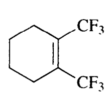
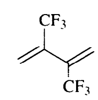
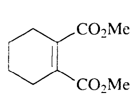
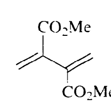
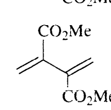
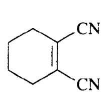
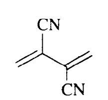
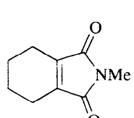
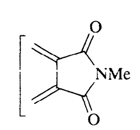
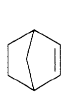
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	280°	C_2H_4 (—) +  (—)	583
	FVP, 920 - 950°	 R = H, Me +  (≥50)	584
	FVP, 800°	C_2H_4 (—) +  (44)	585
	FVP, 700 - 800°	C_2H_4 (—) +  (—)	586
	FVP, 600 - 1000°	C_2H_4 (—) +  (8)	587
	FVP, 750 - 800°	C_2H_4 (—) +  (90)	587
	FVP, ≥ 650°	C_2H_4 (—) +  (—)	587
	304 - 398° $k = 1.378 \times 10^{11}\, e^{-42.750/RT}\, s^{-1}$	C_2H_4 (—) + CP (—)	588
	266 - 304°; $E_a = 43.5$; log A = 13.8	C_2H_4 (—) + CP (—)	292
	GLC, var. inlet temp. $E_a = 41.3$	C_2H_4 (—) + CP (—)	589
	530 - 570°; $E_a = 44.5$ log A = 14.3	C_2H_4 (—) + CP (—)	590
	269 - 1200°, shaker tube	C_2H_4 (—) + CP (—)	591
	pulsed IR laser, SF_6	C_2H_4 (—) + CP (—)	514

TABLE II. ETHYLENE (*Continued*)

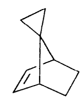
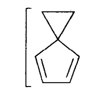
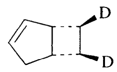
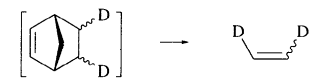
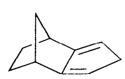
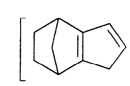
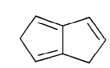
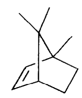
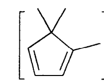
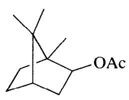
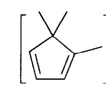
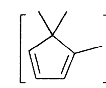
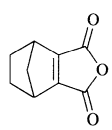
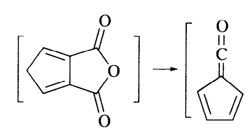
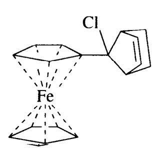
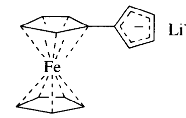
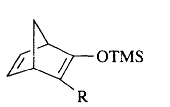
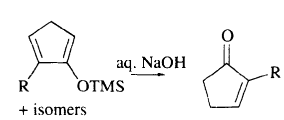
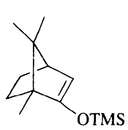
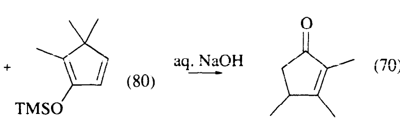
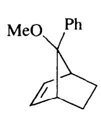
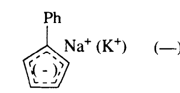
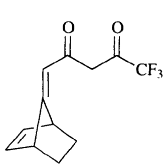
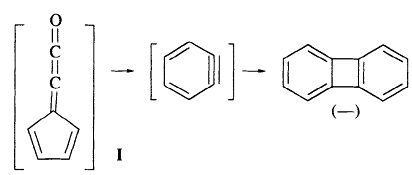
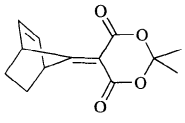
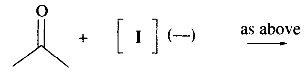
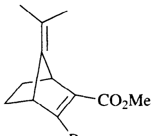
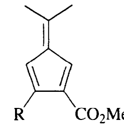
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	pulsed IR laser, SF_6	C_2H_4 (—) +  + benzene, toluene	514
	300°	 (—) + CP (—)	592
	575°	 → C_2H_4 (—) +  (33)	593, 594
	329 - 429° $\Delta H^{\#}$ = 44.7; $\Delta S^{\#}$ = 2.3	C_2H_4 (—) +  (—)	595
 isobornyl acetate	210 - 370°	C_2H_4 (—) +  (—)	596
	pulsed laser	C_2H_4 (—) +  (—)	597
	FVP, 550°	C_2H_4 (—) +  → red polymer	598
	Li, rt	C_2H_4 (—) + 	245
	600°	C_2H_4 (—) +  R / (%): H 95; Me 90; allyl 80; *n*-pentyl 90	579
	—	C_2H_4 (—) + 	579
	Na-K, rt	C_2H_4 (—) +  (—)	248
	FVP, 700°	C_2H_4 (—) + 	599
	FVP, 600°	C_2H_4 (—) + 	599
	FVP, 580°	C_2H_4 (—) +  R / (%): H 68; CO_2Me 99	600

TABLE II. ETHYLENE (*Continued*)

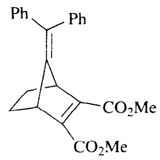
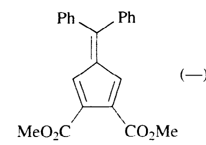
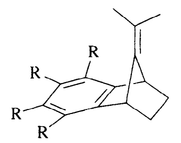
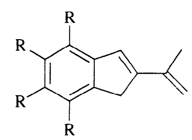
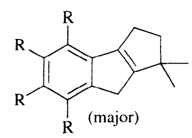
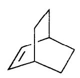
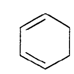
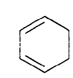
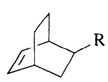
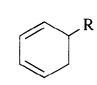
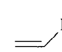
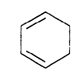
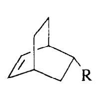
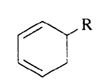
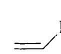
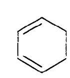
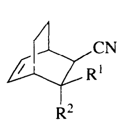
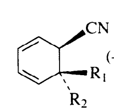
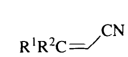
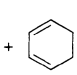
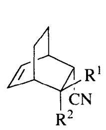
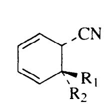
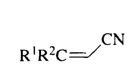
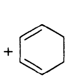
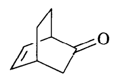
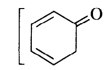
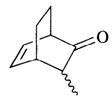
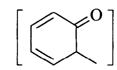
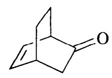
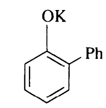
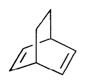
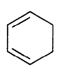
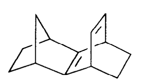
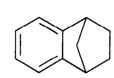
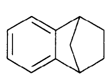
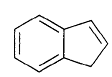
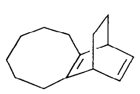
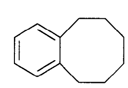
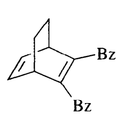
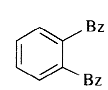
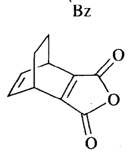
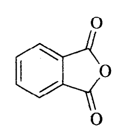
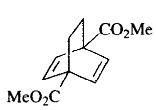
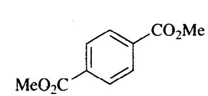
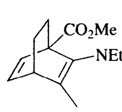
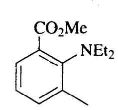
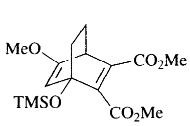
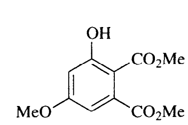
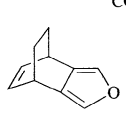
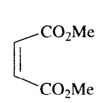
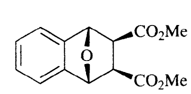
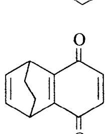
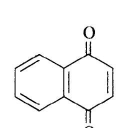
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	200°	C_2H_4 (—) +  (—)	601
	FVP, 600°	C_2H_4 (—) +  +  (major) R (%): H 23; F 13; Cl 12	602, 603
	376 - 445°; E_a = 58.4	C_2H_4 (—) +  (—)	604
	275 - 359° E_a = 57.3; log A =15.1	C_2H_4 (—) +  (—)	309
 *exo*	318 - 422°	→ C_2H_4 (—) +  (—) R / E_a: Me 59.3; Et 59.9; *i*-Pr 59.0 →  (—) +  (—) R / E_a: Me 59.2; Et 59.0; *i*-Pr 59.2	312
 *endo*	294 - 397°	→ C_2H_4 (—) +  (—) R / E_a: Me 57.8; Et 57.7; *i*-Pr 57.9 →  (—) +  (—) R / E_a: Me 58.2; Et 58.4; *i*-Pr 57.5	Refs. 312
	245 - 357°	→ C_2H_4 (—) +  (—) R^1 / R^2 / E_a: H H 57.4; Me H 59.0; H Me 58.2 →  (—) +  (—) R^1 / R^2 / E_a: H H 54.6; Me H 53.5; H Me 53.2	313
	245 - 357°	→ C_2H_4 (—) +  (—) R^1 / R^2 / E_a: H H 58.5; Me H 56.2; H Me 56.6 →  (—) +  (—) R^1 / R^2 / E_a: H H 54.3; Me H 52.0; H Me 53.5	313

TABLE II. ETHYLENE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 800°	C_2H_4 (—) +  (—)	605
	FVP, 800°	C_2H_4 (—) +  (—)	605
	KOBu-*t*	2 C_2H_4 (—) +  (—)	235
	81 - 162°; E_a = 32.5 log A = 14.1	C_2H_4 (—)[a] + benzene (—)	281
 + C_2H_2	179 - 319°; E_a = 27.2 log A = 7.5[b]	C_2H_4 (—) + benzene (—)	281
	heat	C_2H_4 (—) +  (—)	606, 607
	FVP, 800°	C_2H_4 (—) +  (100)	329
	163°	C_2H_4 (90) +  (63)	608
	160°, 2 h	C_2H_4 (—) +  (99)	297
	60°	C_2H_4 (—) +  (—)	609
	50 - 80°; $\Delta H^{\#}$ = 26.8 $\Delta S^{\#}$ = 0.4	C_2H_4 (—) +  (—)	286
	140°	C_2H_4 (—) +  (75)	610
	1. 120°, 12 h 2. SiO_2 chrom.	C_2H_4 (—) +  (71)	611
 + 	61°, 20 h	C_2H_4 (—) +  (70)	612
	130 - 180°	C_2H_4 (—) +  (—)	314

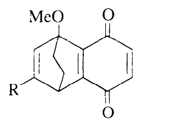
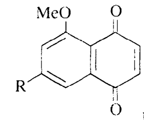
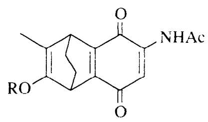
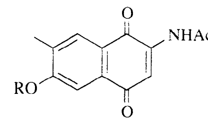
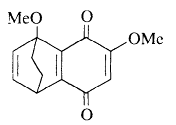
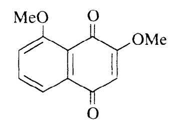
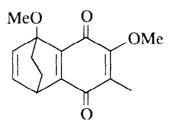
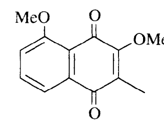
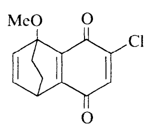
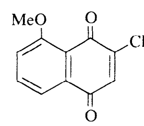
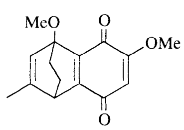
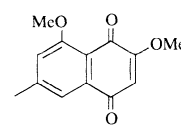
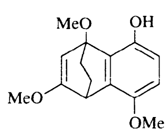
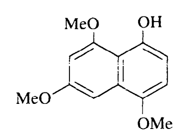
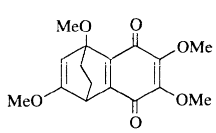
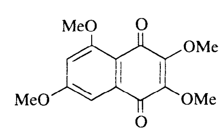
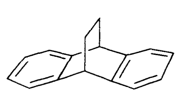
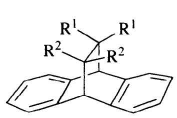
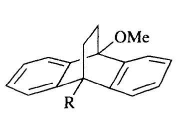
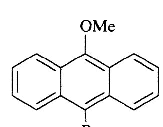
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	120 - 160°	C_2H_4 (—) +  (—) R = H or OMe	613
 R = TBDMS	heat	C_2H_4 (—) +  (—)	614
	120°	C_2H_4 (—) +  (98)	615
	115°	C_2H_4 (—) +  (94)	616
	115°	C_2H_4 (—) +  (100)	616
	115°	C_2H_4 (—) +  (92)	616
	160°	C_2H_4 (—) +  (75)	617
	150°	C_2H_4 (—) +  (—)	618
	229 - 278°; $\Delta H^{\#}$ = 45.2 $\Delta S^{\#}$ = 3.2[c]	C_2H_4 (—) + $C_{14}H_{10}$ (—)	310
 R^1 R^2 k_{rel}(219°) H H 1 D H 0.924 ± 0.005 D D 0.852 ± 0.007		$C_2(H,D)_4$ (—) + $C_{14}H_{10}$ (—)	310
 R k_{rel}[d] H 1 SPh 4.3 (3.9) CHO 6.4 (5.3 CN 19.1 (10.7)	*ca.* 225°, neat (melt)	C_2H_4 (—) +  (—)	619

TABLE II. ETHYLENE (*Continued*)

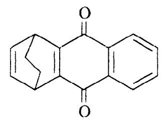
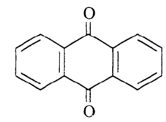
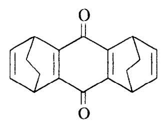
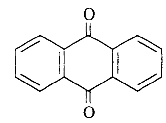
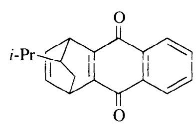
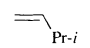
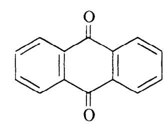
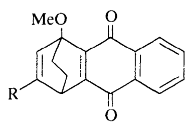
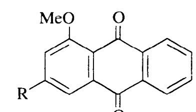
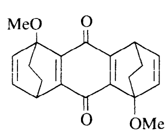
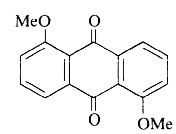
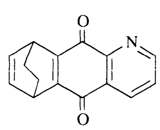
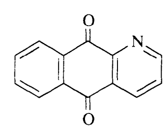
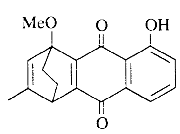
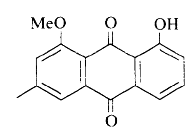
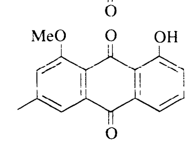
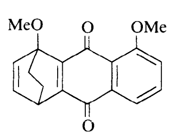
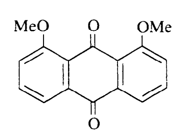
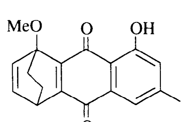
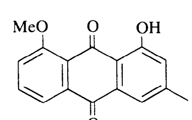
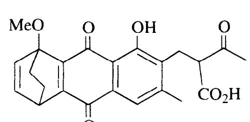
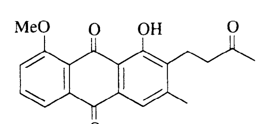
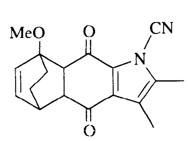
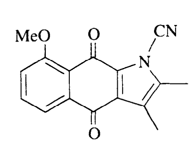
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	180 - 190°	C_2H_4 (—) +  (—)	314
	180°	C_2H_4 (—) +  (—)	314
	150°	 (—) +  (—)	314
	sublime, 0.5 Torr	C_2H_4 (—) +  (—) R = H or OMe	613
	190 °	C_2H_4 (—) +  (—)	613
	220°	C_2H_4 (—) +  (—)	613
	250°	C_2H_4 (—) +  (82)	620
	heat	C_2H_4 (—) +  (80)	618
	heat	C_2H_4 (—) +  (—)	618
	160°	C_2H_4 (—) +  (—)	621
	160°	C_2H_4 (—) +  (82)	621
	heat, (oxidation)	C_2H_4 (—) +  (—)	622

TABLE II. ETHYLENE (*Continued*)

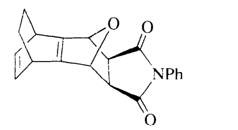
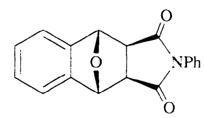
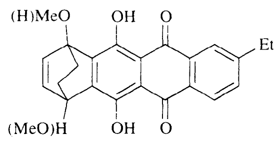
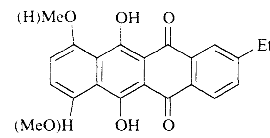
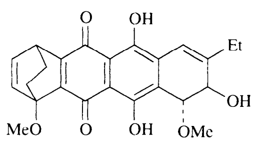
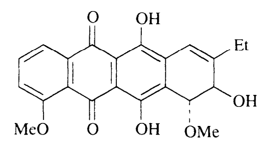
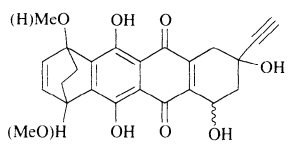
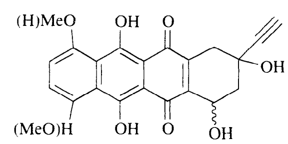
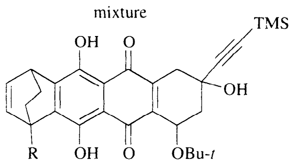
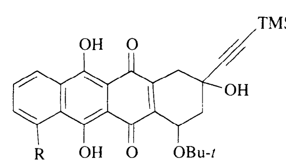
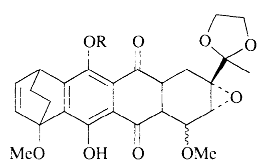
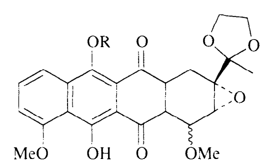
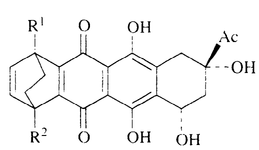
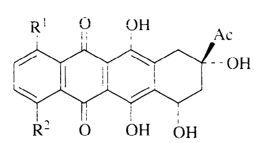
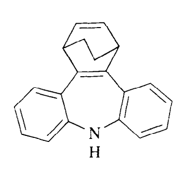
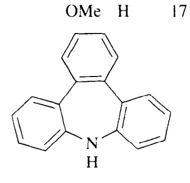
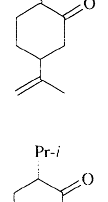
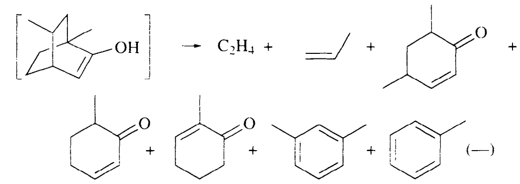
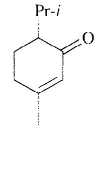
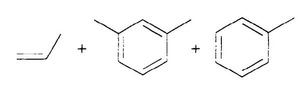
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 *exo, exo* (75) + *endo, exo* (25)	160°, 5 min	C_2H_4 (—) +  (100)	612
 mixture	155°	C_2H_4 (—) +  (52) *syn:anti* = 80:20	623
	155°	C_2H_4 (—) +  (≥ 90)	624
 mixture	145°	C_2H_4 (—) +  (89)	625
	145°	C_2H_4 (—) +  R = H (91), R = OMe (74)	626
 R = pivaloyl	135°	C_2H_4 (—) +  (—)	627
 R^1, R^2 = H, OMe (mixture)	140°	C_2H_4 (—) +  R^1 / R^2 / (%): H / OMe / 32 (daunomycinone); OMe / H / 17	628
	158°	C_2H_4 (—) +  (—)	629
	400°	 (—)	630
	400°	C_2H_4 +  (—)	631

TABLE II. ETHYLENE (*Continued*)

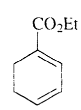
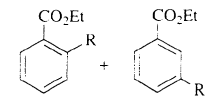
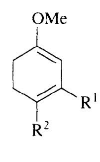
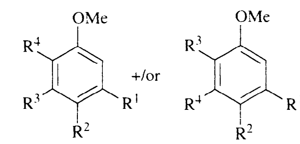
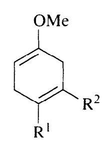
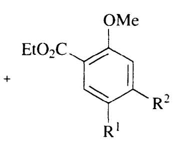
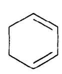
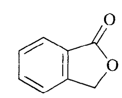
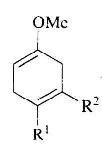
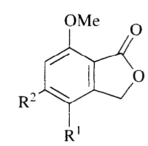
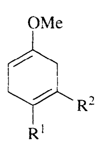
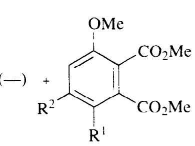
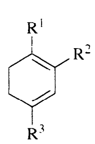
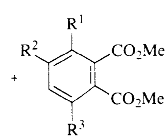
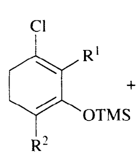
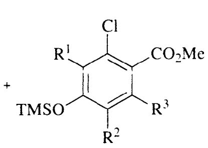
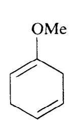
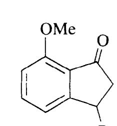
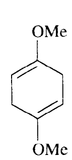
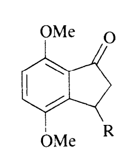
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + ≡—R	320°	C_2H_4 (—) +  I + II R | I:II | (%) Ph | 3.4:1 | 30 CO_2Et | 0.96:1 | 21 Me | 1:3.2 | 7	632
 + R^3—≡—R^4 R^1 = H, Me, or OMe R^2 = H, Me, OMe, or C_8H_{17} R^3 = Me, *n*-Bu, or *n*-pentyl R^4 = CO_2Me or CO_2Et	180 - 200°	C_2H_4 (—) +  (—)	633
 + ≡—CO_2Et	100°, catalyst **A** or **B** **A** = dichloroMA **B** = tris[(Ph)$_3$P]$_3$RhCl	C_2H_4 (—) +  R^1 | R^2 | cat. | (%) H | H | A | 56 OMe | H | A | 63 Me | H | A | 55 H | OMe | B | 15	634
 + $HOCH_2$—≡—CO_2Me	100°	C_2H_4 (—) +  (61)	634
 + $HOCH_2$—≡—CO_2Me	100°, catalyst **B**	C_2H_4 (—) +  R^1 | R^2 | (%) H | H | 55 OMe | H | 39 Me | H | 45	634
 + DMAD	heat, catalyst **A** or **B** **A** = dichloroMA **B** = tris[(Ph)$_3$P]$_3$RhCl	C_2H_4 (—) +  R^1 | R^2 | Temp | Time | cat. | (%) H | H | 130° | 1 h | A | 70 OMe | H | 140° | 1 h | A | 67 Me | H | 140° | 10 h | A | 45 H | OMe | 140° | 1 h | A | 63 H | Me | 140° | 18 h | B | 45	634
 + DMAD	112°	C_2H_4 (—) +  R^1 | R^2 | R^3 | (%) H | OTMS | H | 74 (as OH) OTMS | H | Me | 88 H | OTMS | Me | 85 (as OH)	635
 + R^3—≡—CO_2Me	70 - 145°	C_2H_4 (—) +  R^1 | R^2 | R^3 | (%) allyl | H | CO_2Me | 37 H | H | CO_2Me | 12 allyl | Me | CO_2Me | 53 Me | H | H | 61 allyl | H | H | 29	636
 + RCHOH—≡—CO_2Me	100°, [(Ph)$_3$P]$_3$RhCl	C_2H_4 (—) +  R | (%) Ph | 44 *o*-anisyl | 41 2,5-dimethoxyphenyl | 47 3,5-dimethoxyphenyl | 36	637
 + RCHOH—≡—CO_2Me	100°, [(Ph)$_3$P]$_3$RhCl	C_2H_4 (—) +  (36) R = 2,5-dimethoxyphenyl	637

TABLE II. ETHYLENE (*Continued*)

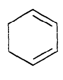
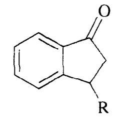
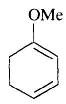
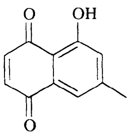
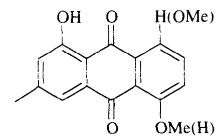
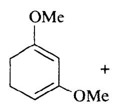
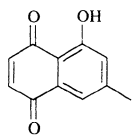
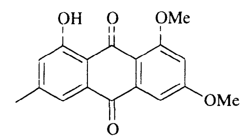
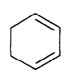
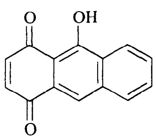
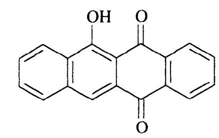
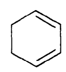
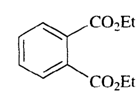
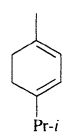
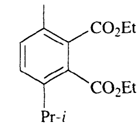
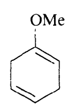
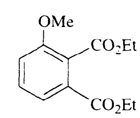
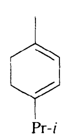
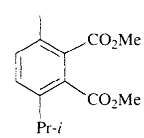
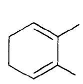
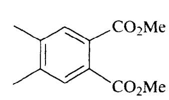
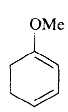
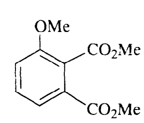
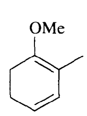
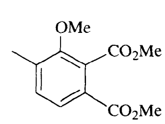
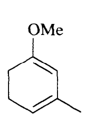
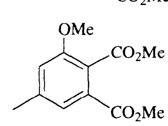
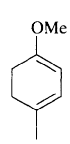
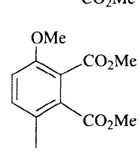
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + RCHOH—≡—CO_2Me	100°	C_2H_4 (—) +  R (%): Ph 42; *o*-anisyl 31	637
 + 	160° (oxid.)	C_2H_4 (—) +  (70)	638
 + 	160° (oxid.)	C_2H_4 (—) +  (62)	638
 + 	heat (oxid.)	C_2H_4 (—) +  (—)	639
 + EtO_2C—≡—CO_2Et	200°	C_2H_4 (—) +  (—)	132
 + EtO_2C—≡—CO_2Et	160–170°	C_2H_4 (—) +  (—)	315
 + EtO_2C—≡—CO_2Et	125°, dichloro MA	C_2H_4 (—) +  (—)	640
 + DMAD	120–150°	C_2H_4 (—) +  (—)	641, 316
 + DMAD	pyrolyze	C_2H_4 (—) +  (—)	642
 + DMAD	*ca.* 200°	C_2H_4 (—) +  (—)	643
 + DMAD	*ca.* 200°	C_2H_4 (—) +  (—)	643
 + DMAD	*ca.* 200°	C_2H_4 (—) +  (—)	643
 + DMAD	*ca.* 200°	C_2H_4 (—) +  (—)	643

TABLE II. ETHYLENE (*Continued*)

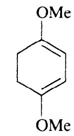
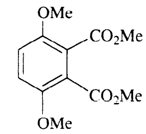
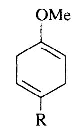
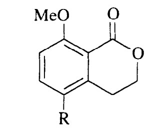
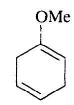
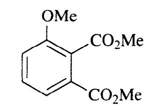
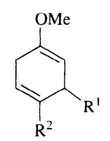
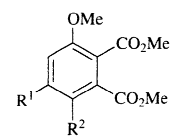
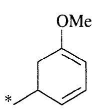
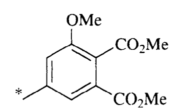
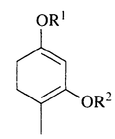
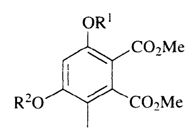
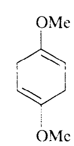
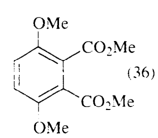
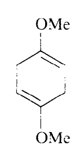
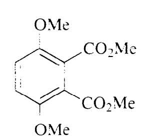
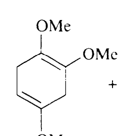
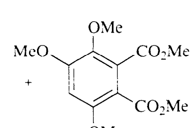
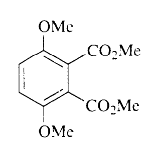
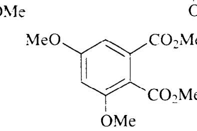
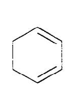
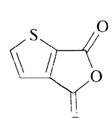
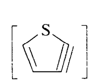
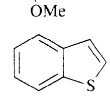
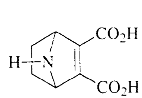
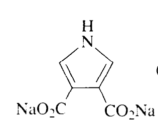
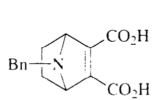
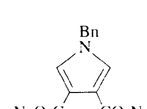
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	*ca.* 200°	C_2H_4 (—) +  (—)	643
 + THPO$(CH_2)_2$—≡—CO_2Me	180°	C_2H_4 (—) +  R (%): H 65; Me 67	644
 + DMAD	heat, TFA catalyst	C_2H_4 (—) +  (—)	320
 + DMAD	140 - 200°, dichloroMA cat.	C_2H_4 (—) +  R^1 R^2 (%): H H 90; OMe H —; H OMe —; Me H —; H Me —	321
 + DMAD * = $^{14}CH_3$	200°	C_2H_4 (—) +  (74)	645
 + DMAD R^1 = allyl; R^2 = TMS	120°	C_2H_4 (—) +  (59)	646
 + DMAD	heat	C_2H_4 (—) +  (36)	647
 + DMAD	heat	C_2H_4 (—) +  (36)	647
 + DMAD	heat	C_2H_4 (—) +  (2) +  (3) +  (4)	647
 vapor + 	FVP, 500°	 → C_2H_4 (—) +  (14)	543
	aq. NaOH, 100°	C_2H_4 (—) +  (7)	241
	aq. Na_2CO_3, 100°	C_2H_4 (—) +  (—)	239

TABLE II. ETHYLENE (*Continued*)

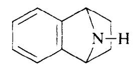
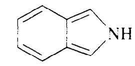
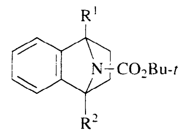
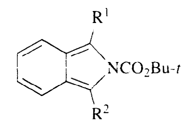
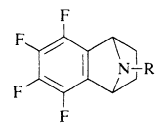
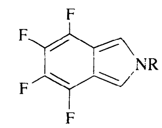
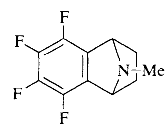
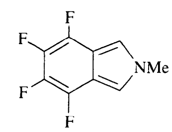
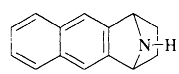
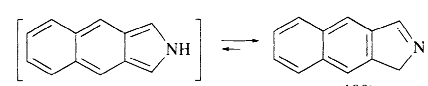
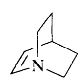
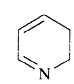
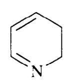
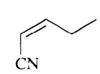
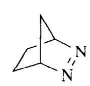
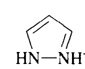
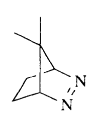
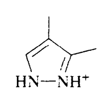
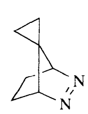
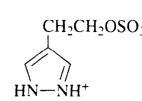
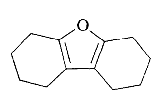
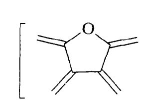
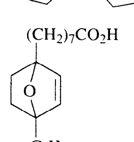
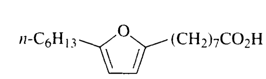
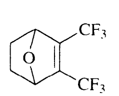
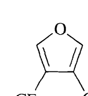
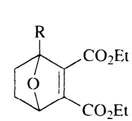
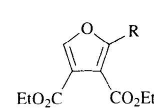
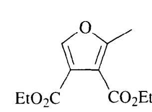
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 600°	C_2H_4 (—) +  (—)	648, 649
 R¹ R²: H H; H Me; Me Me	FVP, 600°	C_2H_4 (—) +  (—)	650
 R = H or Bn	FVP, 550°	C_2H_4 (—) +  (100)	651
	120°, 1 wk.	C_2H_4 (—) +  (100)	603
	FVP, 600°	C_2H_4 (100) +  (100)	652, 653
	FVP, 520°	C_2H_4 (—) +  (70)	498, 654
	FVP, ≥ 600°	 (—)	654
	conc H_2SO_4, 120°, 1 h	C_2H_4 (—) +  (—)	201
	conc H_2SO_4, 120°, 1 h	C_2H_4 (—) +  (100)	201
	conc H_2SO_4, 120°, 1 h	C_2H_4 (—) +  (—)	201
	FVP, 920 - 950°	C_2H_4 (—) +  (—) decomp. ≥ -40°	323
	160 -180°	C_2H_4 (—) +  (86)	655
	400°	C_2H_4 (—) +  (100)	553
 R = H or Me **I**	145 -165°	C_2H_4 (—) +  (—)	656
I, R = Me	180°	C_2H_4 (—) +  (86)	657

TABLE II. ETHYLENE (*Continued*)

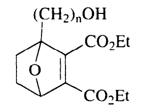
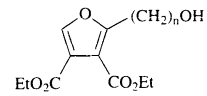
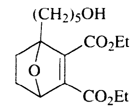
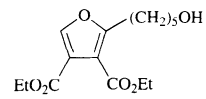
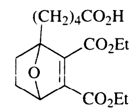
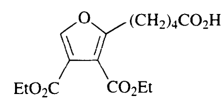
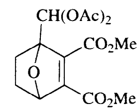
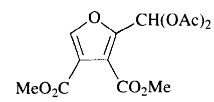
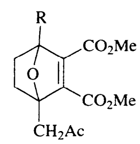
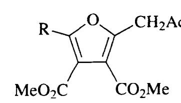
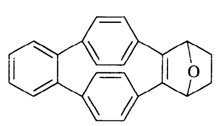
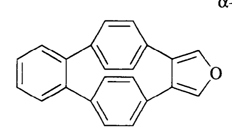
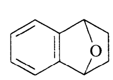
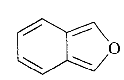
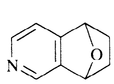
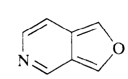
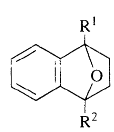
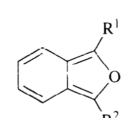
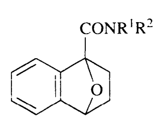
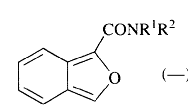
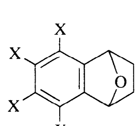
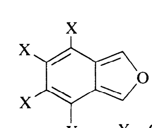
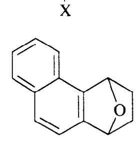
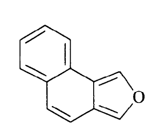
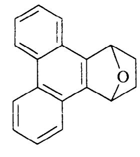
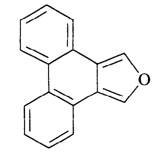
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	175 - 200°, 16 Torr	C_2H_4 (—) +  n = 3 (86) n = 4 (68)	658
	200°, vac.	C_2H_4 (—) +  (—)	660
	200°, vac.	C_2H_4 (—) +  (68)	661
	200°	C_2H_4 (—) +  (—)	662
	200°	C_2H_4 (—) +  R (%): Me 95; Et 75; Bn 70; $Ph(CH_2)_2$ 74; $PhCH_2CH(Et)$ 65; $(Bn)_2CH$ 71; α-naphthyl$(CH_2)_2$ 66	663
	220°, 0.5 Torr	C_2H_4 (—) +  (92)	664
	FVP, 650°	C_2H_4 (—) +  (100)	322, 665
	FVP, 650°	C_2H_4 (—) +  (—)	666
	FVP, 600°	C_2H_4 (—) +  (—) R^1 R^2: Bn H; Me H; Me Me	667
 R^1 R^2: Me Me; Et Et; $-(CH_2)_4-$; $-(CH_2)_5-$; $-(CH_2)_2O(CH_2)_2-$	pyrolysis	C_2H_4 (—) +  (—)	668
	FVP, 600°	C_2H_4 (—) +  (100) X = Cl or F	603
	FVP, 520°	C_2H_4 (—) +  (95)	669, 670
	FVP, 520°	C_2H_4 (—) +  (95)	669, 670

TABLE II. ETHYLENE (*Continued*)

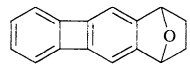
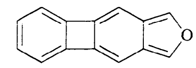
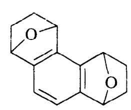
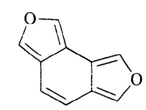
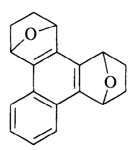
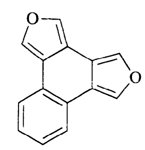
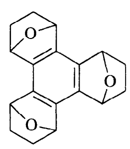
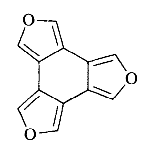
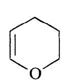
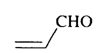
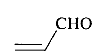
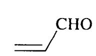
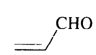
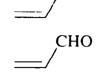
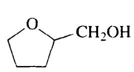
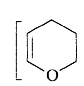
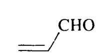
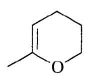
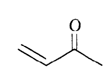
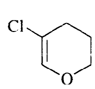
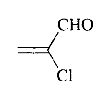
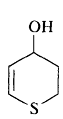
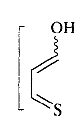
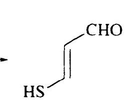
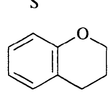
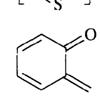
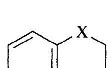
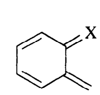
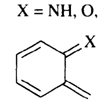
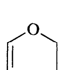
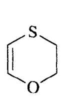
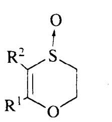
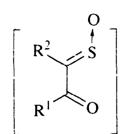
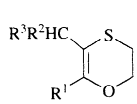
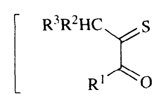
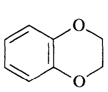
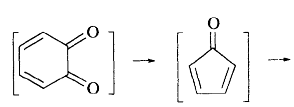
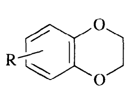
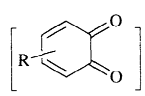
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP	C_2H_4 (—) +  (—)	670
	FVP	C_2H_4 (—) +  (—)	670
	FVP, 560°	C_2H_4 (—) +  (100)	670
	FVP, 550°	C_2H_4 (—) +  (100)	670
	316 - 389°; E_a = 42.4	C_2H_4 (—) +  (—)	324
	500 - 540°	C_2H_4 (88) +  (85)	671
	600°	C_2H_4 (—) +  (63)	672, 673
	450°, alumina-silica	C_2H_4 (—) +  (62)	194
	pulsed laser, SiF_4	C_2H_4 (—) +  (—)	513
	heat, silica-alumina	 → C_2H_4 (—) +  (≥ 62)	193
	330 - 370°; E_a = 51.2	C_2H_4 (—) +  (—)	325
	heat	C_2H_4 (—) +  (—)	673
	FVP	C_2H_4 (—) +  →  (—)	330, 331
	413°	C_2H_4 (—) +  (—)	674
	500 - 750°	C_2H_4 (—) +  (—) X = NH, O, or S	327
	FVP, 1000°	C_2H_4 (—) +  (—) X = NH, O, or S	328
	heat; E_a = 52.9	C_2H_4 (—) + OHC-CHO (—)	326
	pulsed laser	C_2H_4 (—) + OHC-CHO (—)	675
	FVP, 720°	C_2H_4 (—) + [OHC-CHS] (—)	676, 331

TABLE II. ETHYLENE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 750°	C_2H_4 (—) +  (—)	331
 R[1] R[2] R[3] H H H H Me Me Me H H	850°	C_2H_4 (—) +  (—) R[1] R[2] R[3] H H H polymerizes ≥ -150 °[a] H Me Me tautomerizes	677
	FVP, 600°	C_2H_4 (—) +  → DA dimer	329
	pulsed laser	C_2H_4 (—) +  (—)	678

[a] No C_2H_2 was detected; loss of C_2H_4 was ≥ 10^6 faster than loss of C_2H_2.

[b] The DA reaction (2nd order) is the rate determining step in this sequence.

[c] This value was recalculated as per Ref. 130, footnote 32.

[d] This value was calculated from single data points listed in this reference; numbers in () are the k_{rel} values given in the reference, but correlation with the data points is not shown.

TABLE III. MONOALKYLETHYLENES

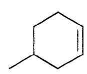
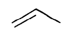
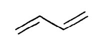
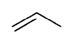
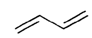
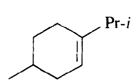
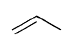
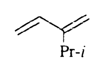
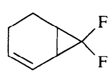
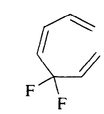
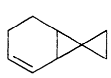
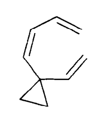
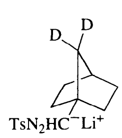
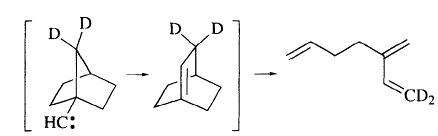
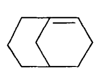
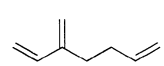
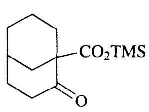
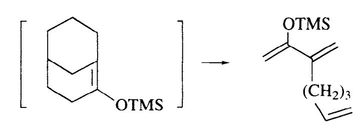
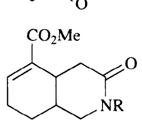
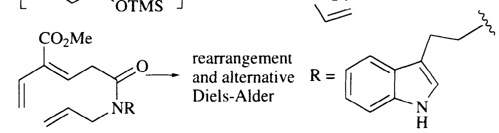
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	627 - 877°, shaker tube E_a = 66.6; log A = 15.1	 (—) +  (—)	333
	690°	 ("some") +  (56)	561
	655°	 (73) +  (—)	576
	177°; ΔG° = 0.43 ΔH# = 35.6; ΔS# = −0.4	 (—)	679
	188 - 214°; ΔG° = −2.54 ΔH# = 35.0; ΔS# = −3.3	 (—)	679
	330°	 (31)	680
	heat[a]	 (—)	681
	FVP, 550 - 750°	 (3–75)	682
	112° (⇌)		683

TABLE III. MONOALKYLETHYLENES (*Continued*)

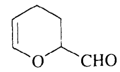
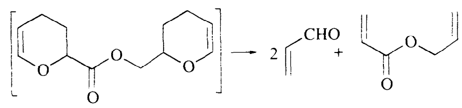
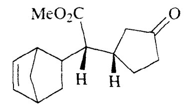
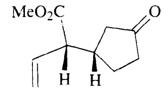
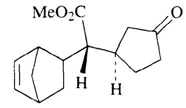
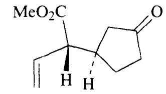
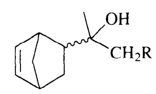
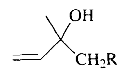
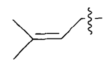
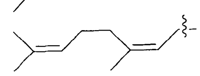
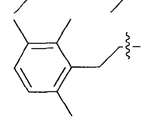
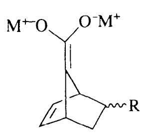
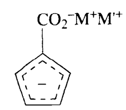
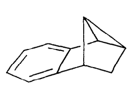
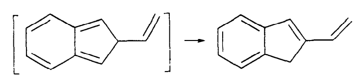
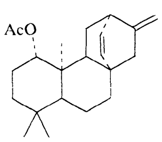
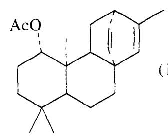
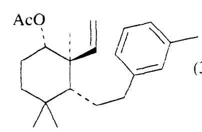
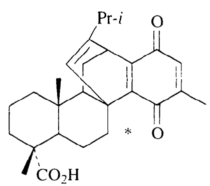
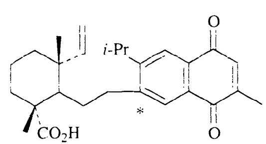
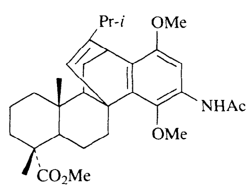
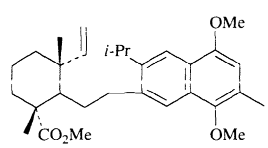
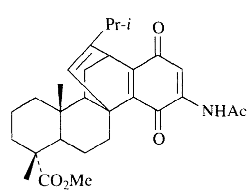
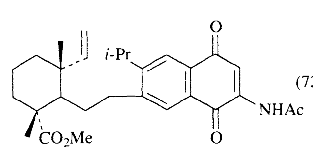
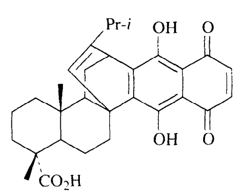
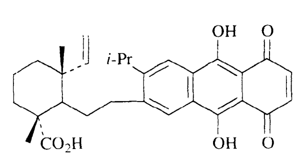
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Al(OPr\text{-}i)_3$, heat	 (—)	684
	FVP, 500°	 (100) 100% de + CP	685
	FVP, 500°	 (100) 100% de + CP	685
	FVP, 550°	 + CP R (%) Me 96  98  96  99	686
 R = *n*-hexyl	$k_K > k_{Li}$ $M^+, M'^+ =$ K or Li $M^+ = M'^+ =$ Li $t_{1/2}(40°) = 20$ h	 (—) + 1-octene (—)	236
	FVP, 400°	 (100)	687
	TsOH, pyridine, 112°	 (17) +  (30)	688
	DMF, 150°	 (45)	689
	DMF, 150°	 (80)	689
	DMF, 150°	 (72)	689
	DMF, 150°	 including tautomer (82)	689

TABLE III. MONOALKYLETHYLENES (*Continued*)

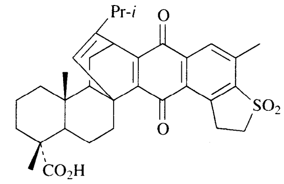
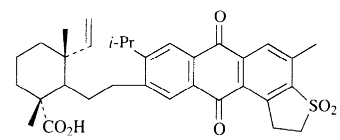
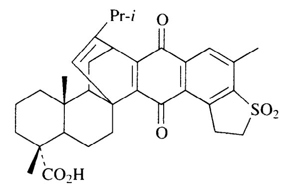
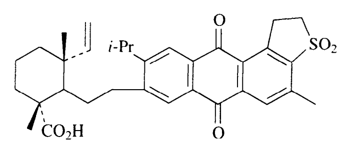
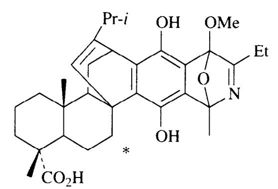
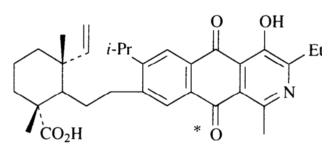
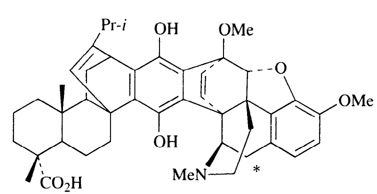
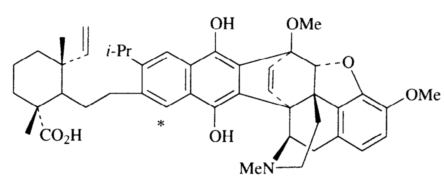
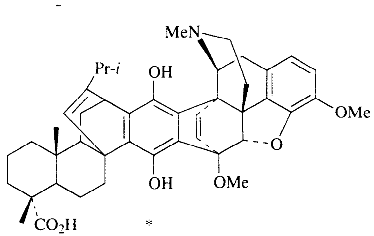
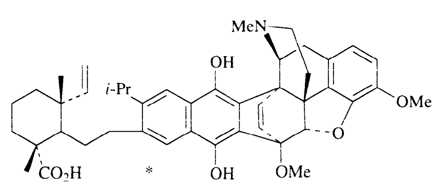
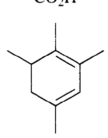
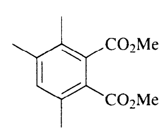
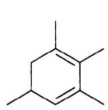
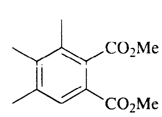
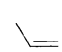
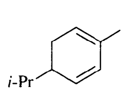
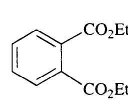
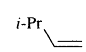
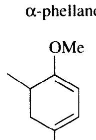
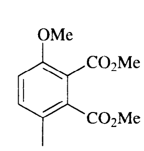
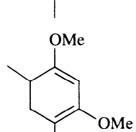
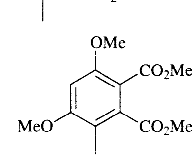
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	DMF, 150°	 (82)	689
	DMF, 150°	 (80)	689
	150°	 (—)	690
	150°	 (53)	690
	150°	 (66)	690
 + DMAD	120 - 150°	 (—) +  (—)	641
 + DMAD	120 - 150°	 (—) +  (—)	641
 + EtO_2C—≡—CO_2Et α-phellandrene	200°	 (—) +  (—)	132
 + DMAD	190°	 (—) + (—)	691
 + DMAD + 1,4-diene isomer	190°	 (—) + (—)	691

TABLE III. MONOALKYLETHYLENES (*Continued*)

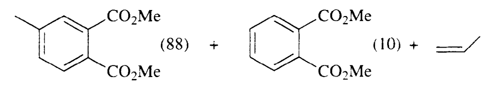
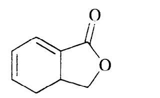
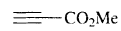
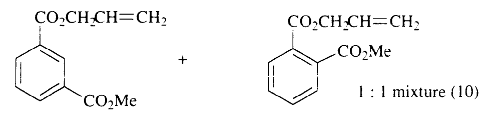
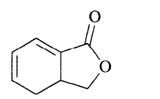
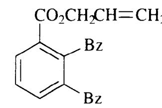
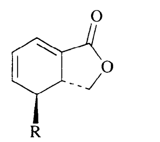
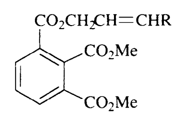
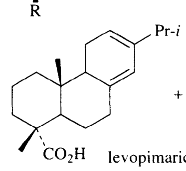
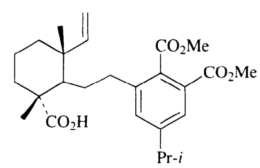
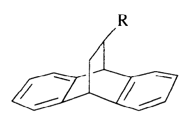
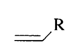
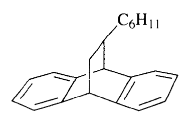
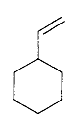
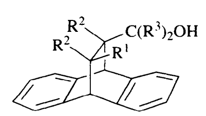
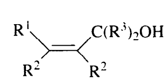
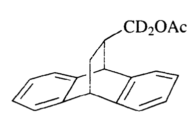
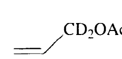
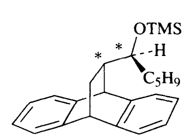
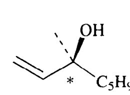
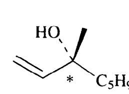
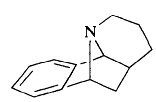
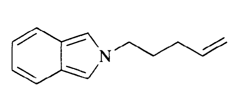
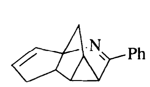
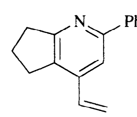
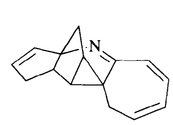
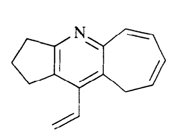
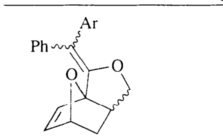
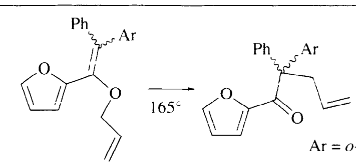
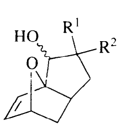
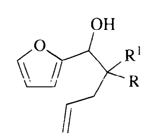
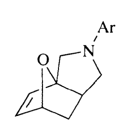
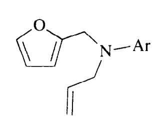
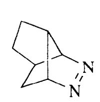
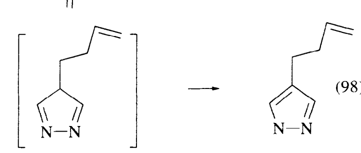
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
$(K^+)_2$ $(COT)^{-2}$	1. 2 MeI 2. DMAD 3. 195°, 0.5 h		692
 + 	140°, 40 h		693
 +	140°, 40 h	 (46)	693
 + DMAD	140°, 40 h	 R (%): H 45; Ph 62	693
 levopimaric acid + DMAD	190°	 (—)	694, 317
	250°	 + $C_{14}H_{10}$ (—) kinetic study; R = H, Me, Et, *i*-Pr, *t*-Bu	175, 176
	330 - 390°	 (98) + $C_{14}H_{10}$ (—)	695
	290 - 300°	 + $C_{14}H_{10}$ (—)	696
		R^1 R^2 R^3 (%): H D H 71; H H D 98; D H D 52; H D D 87	
	360°	 (88) + $C_{14}H_{10}$ (—)	697
 *R,S* diastereomer	1. FVP, 660° 2. hydrolysis	 (89) + $C_{14}H_{10}$ (—)	698
R,R diastereomer	1. FVP, 660° 2. hydrolysis	 (95) + $C_{14}H_{10}$ (—)	698
	≥ 150°; $K_{eq}(200°) = 2.3$ ⇌	 (—)	699
	FVP, 400°	 (22)	700
	157°, 3 h	 (4)	700

TABLE III. MONOALKYLETHYLENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 mixture of stereoisomers	165° ⇌ 90°	 (95) Ar = o-NHC(O)C_6H_4Bu-*t*	701
	80°, benzene ⇌	 R[1] | R[2] | $K_{eq}(80°)$ | $10^6 k_{rDA}$ H | H | (no DA adduct formed) Me | Me | >20 | not det. —$(CH_2)_5$— | 1.1 | 1.62 *n*-Pr | *n*-Pr | 0.71 | 1.95 —$S(CH_2)_3S$— | 0.31 | 1.86 SEt | SEt | 0.18 | 1.22 OEt | OEt | 0.21 | 3.04	334
 Ar = Ph, *p*-tolyl, *p*-anisyl	vac. distill ⇌ rt, few days	 (—)	336, 335
	FVP, 400°	 (98)	702

[a] The product shown is formed as a byproduct in the pyrolysis of acetate to form starting olefin.

TABLE IV. 1,1-DIALKYLETHYLENES

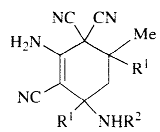
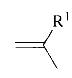
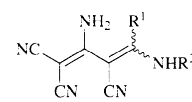
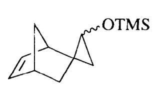
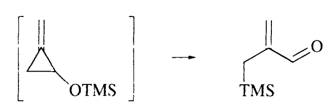
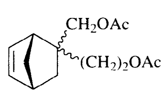
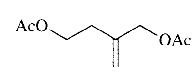
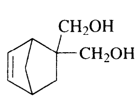
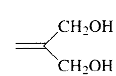
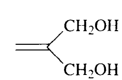
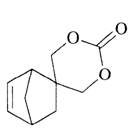
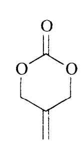
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140°, 1 h	 +  R^1 / R^2 / (%) Me / H / 95 Et / H / 93 Me / NH_2 / 89 Et / NH_2 / 87 Me / Me / 95 Et / Me / 95 Me / Et / 92 Et / Et / 90 Me / Bn / 98 Et / Bn / 94	703
	FVP, 700°	 (—) + CP	704
	270 - 280°	 (>54) + CP	705, 706
	520°	 (63) + CP	707
	235°	 (54) + CP	708
	FVP, 450°	 (92) + CP	709

TABLE IV. 1,1-DIALKYLETHYLENES (*Continued*)

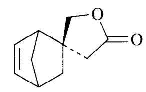
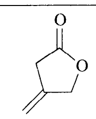
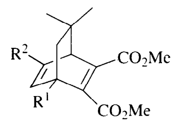
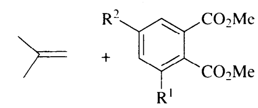
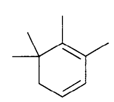
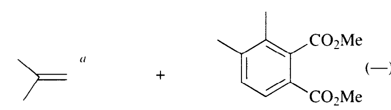
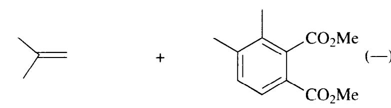
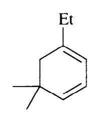
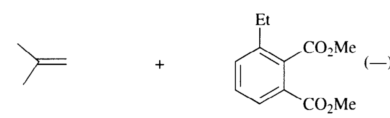
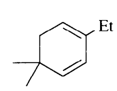
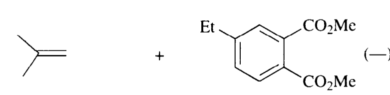
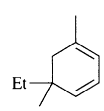
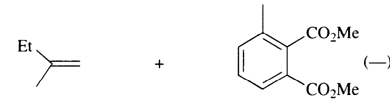
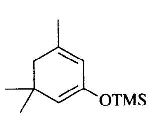
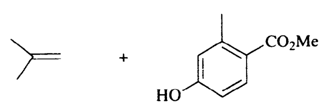
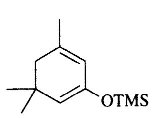
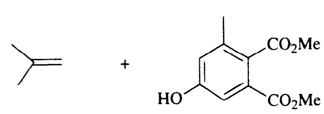
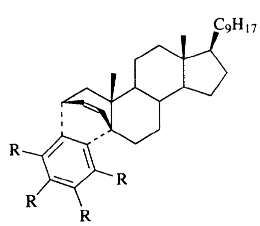
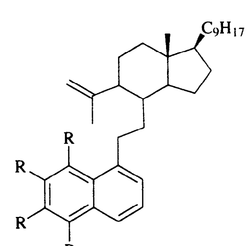
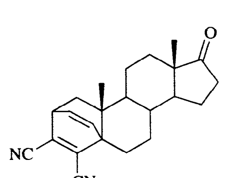
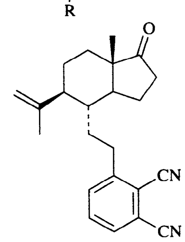
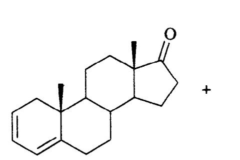
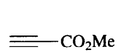
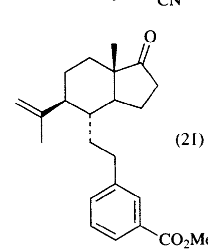
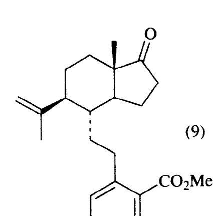
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat	 (100) + CP	710
	200°	 R[1] R[2] (%): OAc, OAc (100); Me, OAc, OAc, Me (—)	711
 + DMAD β-pyrone	heat	 [a] (—)	712, 713
	120 - 150°	 (—)	641
 + DMAD	120 - 150°	 (—)	641
 + DMAD	120 - 150°	 (—)	641
 + DMAD	120 - 150°	 (—)	641
 +	1. 112° 2. H_2O	 (92)	635
 + DMAD	1. 112° 2. H_2O	 (85)	635
	250°	 R (%): H 97; F 64	714
	138°	 (100)	715
 + 	138°	 (21) +  (9)	715

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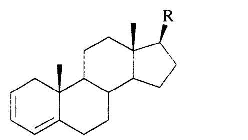
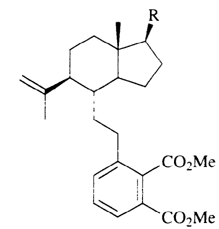
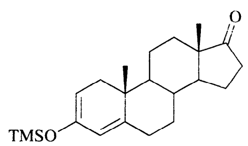
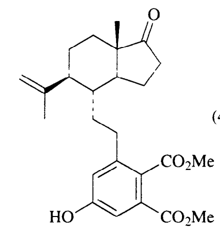
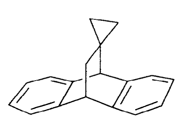
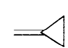
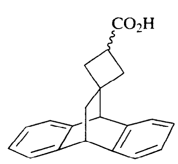
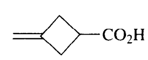
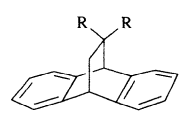
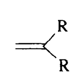
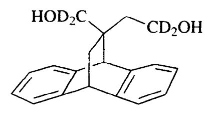
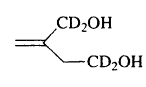
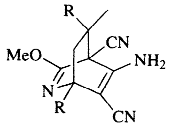
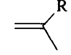
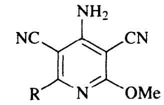
TABLE IV. 1,1-DIALKYLETHYLENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	138°	 R: C_8H_{17} (40); CHCO (30)	715
 + DMAD	138°	 (40)	715
	FVP, 700°	 (100) + $C_{10}H_{14}$ (—)	337, 338
	350°	 (87) + $C_{10}H_{14}$ (—)	338, 716
	350°	 (—) + $C_{10}H_{14}$ (—) R = CH_2OH or CO_2Et	338
	300-350°	 (75) + $C_{10}H_{14}$ (—)	339
	heat	 +  **I**	717

R	Temp	I (%)
Me	140°	99
Et	115°	78
n-Pr	115°	47
i-Pr	115°	83

[a] The isobutylene structure was proven by bromination.

TABLE V. 1,2-DIALKYLETHYLENES

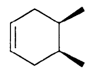
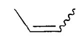
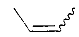
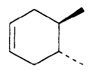
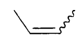
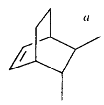
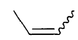
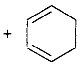
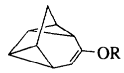
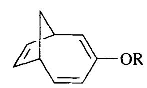
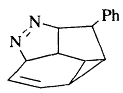
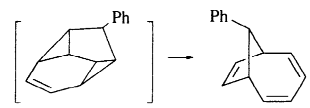
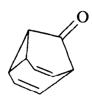
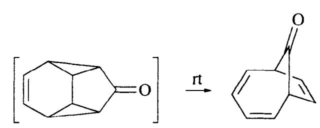
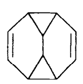
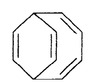
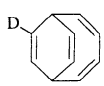
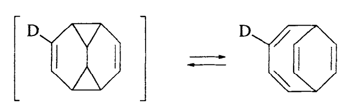
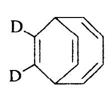
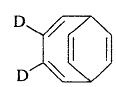
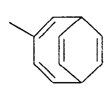
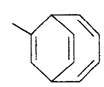
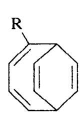
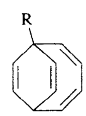
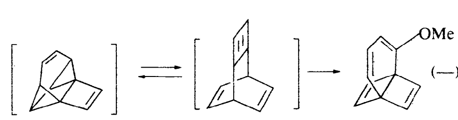
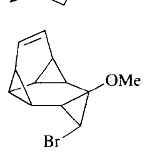
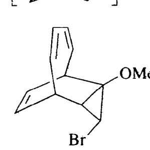
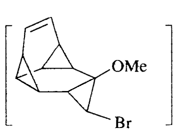
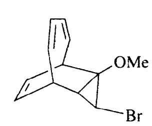
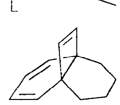
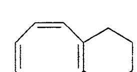
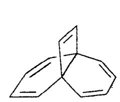
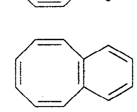
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, gas phase	 (—) $Z{:}E$ = 53.8:3.4	718
	UV, gas phase, Hg sensit.	 (—) $Z{:}E$ = 1.2:3.0	718
	UV, gas phase	 (—) $Z{:}E$ = 2.8:57	718
	UV, gas phase, Hg sensit.	 (—) $Z{:}E$ = 0.6:3.0	718
 [a]	327°	 (—) $Z{:}E$ = 98:2 +  (—)	719
	–52°	 (—) R, $t_{1/2}$ (min): OLi 23; OTMS ≤8	234
	UV	 (40)	720
	1. Br_2 2. Na·Hg	 (54)	721
	–30 to –15°	 (100)	340
	heat ⇌	 (—)	722
	$t_{1/2}$(140°) = 0.5 s ⇌	 (—)	723
	K_{eq}(35°) ≥ 19 $t_{1/2}$ = 24 min	 (—)	341
	K_{eq}(35°)	 (—) R, K_{eq}, $t_{1/2}$ (min): Br 0.43 13; Me 1.07 —; Cl 0.33 24	341
	200°, MeOH ⇌	 (—)	724
	71:29 ⇌	 (—)	725
	0:100	 (—)	725
	430°, flow	 (60)	726, 727
	470°, flow	 (53)	726, 727

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

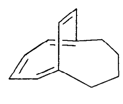
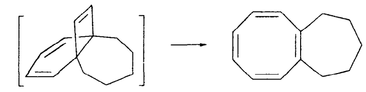
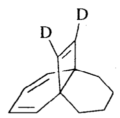
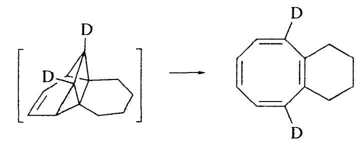
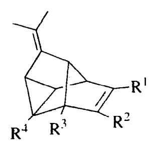
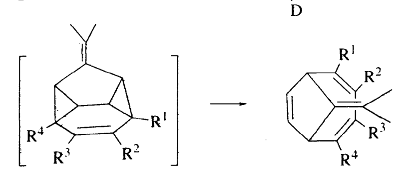
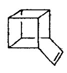
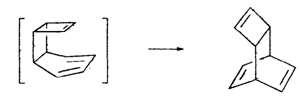
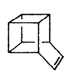
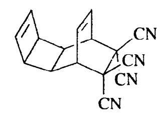
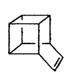
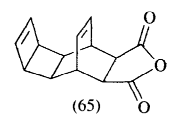
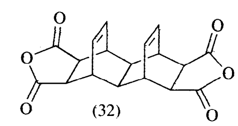
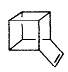
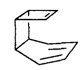
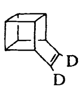
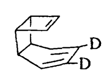
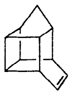
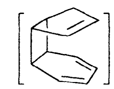
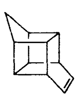
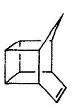
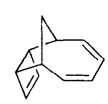
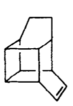
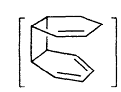
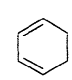
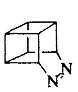
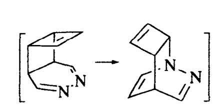
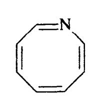
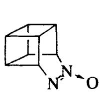
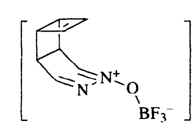
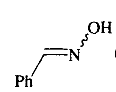
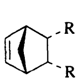
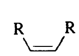
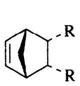
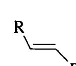
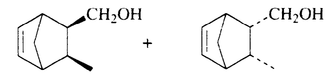
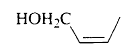
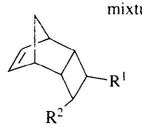
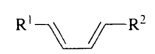
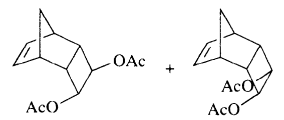
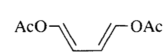
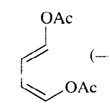
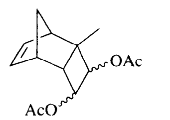
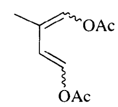
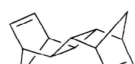
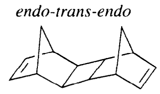
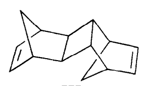
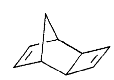
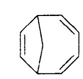
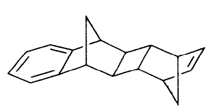
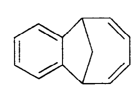
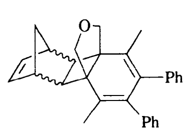
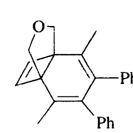
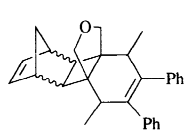
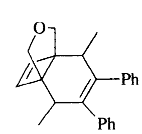
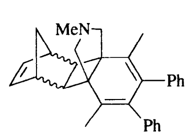
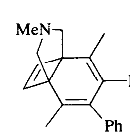
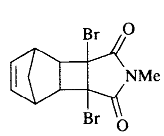
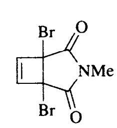
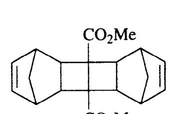
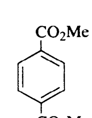
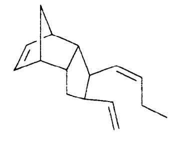
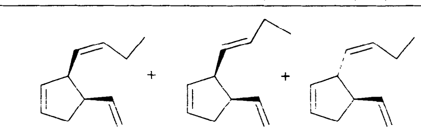
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	485°, flow	 (—)	726, 727
	430°, flow	 (—)	726, 727
 R = H, CO_2Me, or Ph	UV	 (—)	728
 basketene	$t_{1/2}(110°)$ = 34 min E_a = 29.7	 (—) "Nenitzescu's hydrocarbon"	342
 + TCNE	—	 (—)	729
 + MA	65°	 (65) +  (32)	729
	UV, 70°	 (—)	343
	65°	 (—)	730
	≥ 180°; FVP, 370° E_a = 35.3	 $\xrightarrow{b}$ C_6H_6 (—) + CP (—)	346
	80°; E_a = 25.9	C_6H_6 (—) + CP (—)	345
	150°; E_a = 33.2	 (—)	345
	227 - 245° $\Delta H^{\#}$ = 40.5; $\Delta S^{\#}$ = 2.7	 → C_6H_6 (—) +  (—)	347
	FVP, 560°	 → HCN +  (—)	731
	$BF_3 \cdot Et_2O$, 40°	 → →  (—)	215
 R = Me, CH_2OH, or CH_2OAc	FVP, 500°	 (—) + CP	732
 R = Me, CH_2OH, or CH_2OAc	FVP, 500°	 (—) + CP	732

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

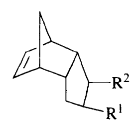
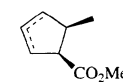
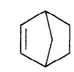
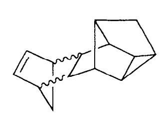
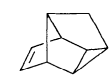
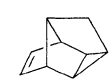
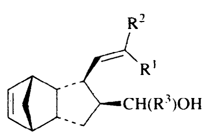
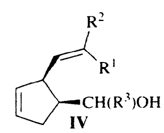
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 mixture, 1 : 3	FVP, 500°	 (100) + CP	733
	FVP, 460°	 + CP (see below)	734
	FVP, 460°	 (—) +  (—) + CP	734
	FVP, 460°	 (—) + CP (—)	735
 **I** *endo-trans-endo*  **II** *endo-trans-exo*  **III** *exo-trans-exo*	280 - 450°[c]	 **IV** *exo* +  **V** + CP	736
	450°	 (88) + CP	737
	FVP	 (—) + CP	738
	FVP	 (—) + CP	738
	FVP	 (—) + CP	738
	FVP, 580°	 (—) + CP	739
	FVP	 (—) + CP	739

Ref. 734 (row 2):

R^1	R^2	(%)
OAc	SPh	100
OCO_2Me	SPh	100
$O_2CCH(OMe)Ph$	Et	93
OAc	OAc	—

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP	 I + II + III + CP	740

Temp	% reac.	I (%)	II (%)	III (%)
450°	35	88	11	1
480°	81	77	21	2
500°	97	69	29	2
510°	—	62	—	—
550°	100	20	64	16

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1, R^2 = Me, CO_2Me and Me, CO_2Me	FVP, 510°	 (100) + CP	740
 mixture from DA reaction of norbornene and CP	240 - 300°, vapor $\Delta H^{\#}$ = 36.2; $\Delta S^{\#}$ = −4	 (—) + CP	364
	450°	 ("good") + CP	736
	550°	 (28) + CP	741
	FVP, 500°	 IV + CP	742

R^1	R^2	R^3	IV (%)
H	H	H	84
Me	H	H	87
Et	H	H	87
Pr	H	H	83
Bu	H	H	84
C_5H_{11}	H	H	78
Me	Me	H	81
Et	H	Me	87

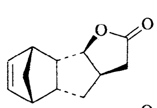
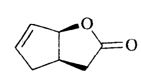
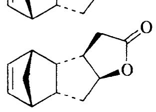
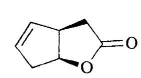
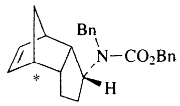
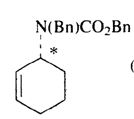
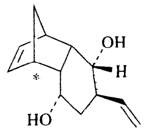
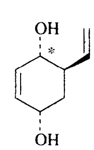
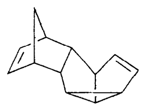
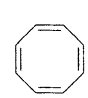
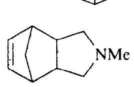
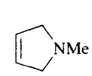
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	300°	 (100) + CP	743
	300°	 (100) + CP	743
	250°	 (98) + CP	744
	250°	 (73) + CP	744, 745
	320°	 (—) + CP	746
	380 - 400°, silicone oil	 (95 crude) + CP	747

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

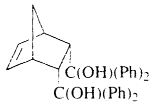
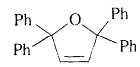
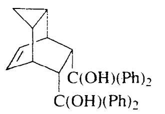
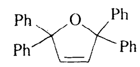
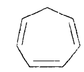
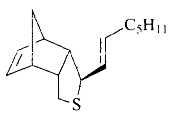
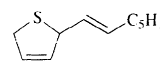
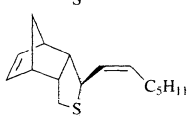
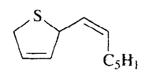
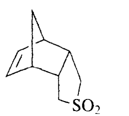
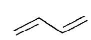
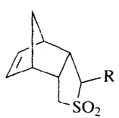
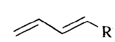
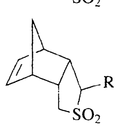
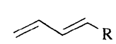
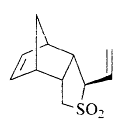
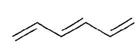
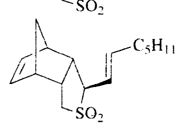
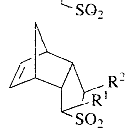
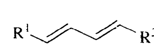
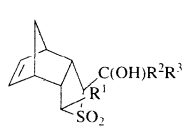
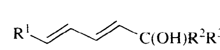
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat	 (97) + CP (55)	748
	heat	 (83) +  (80)	748
	FVP, 600°	 (80) + CP	749
	FVP, 600°	 (42) + CP	749
	FVP, 675°	 (34) + CP (42)	750
	FVP	 + CP R / Temp / (%) / E (%) Me / 650° / 85 / >95 *n*-pentyl / 650° / 90 / >95 (CH$_2$)$_8$OAc / 600° / >41 / ≥97	751
	FVP, 650°	 (25 - 91, 85 - 98% E) + CP R = Me, alkyl, allyl, SnMe$_3$, CO$_2$Et, acyl, CH(OH)R', C(OH)(R')$_2$, (CH$_2$)$_8$OAc	752
	FVP, 600°	 (75, ≥ 98% E) + CP	749
	FVP, 600°	C$_{11}$ trienes (—) + CP five isomers	749
	600 - 650°	 + CP (58 - 96, 91 - 96% E,E) R^1 / R^2 Me / Me *n*-C$_5$H$_{11}$ / *n*-C$_5$H$_{11}$ *n*-C$_5$H$_{11}$ / Et H / TMS Me / TMS *n*-C$_5$H$_{11}$ / TMS Me / (CH$_2$)$_7$OH Et / (CH$_2$)$_8$OAc	753
	650°	 + CP R^1 / R^2 / R^3 / (%) / E (%) H / Me / *n*-Pr / 73 / ≥98 H / —(CH$_2$)$_5$— / / 78 / ≥98 H / H / Et / 77 / ≥98 H / H / *n*-Bu / 73 / ≥98 *n*-Bu / H / Et / 74 / 93 E,E Et / Me / *n*-Pr / — / mixt Me / —(CH$_2$)$_5$— / / — / mixt	754

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

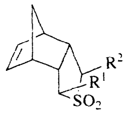
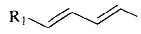
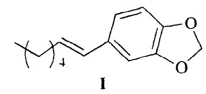
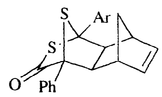
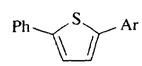
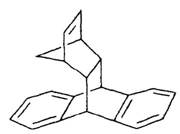
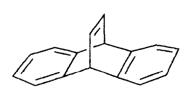
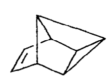
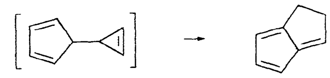
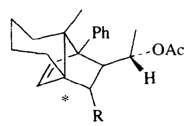
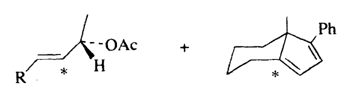
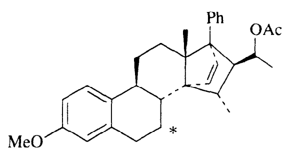
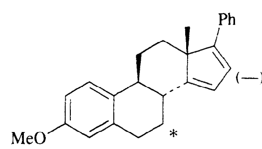
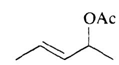
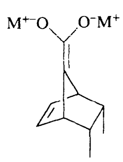
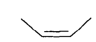
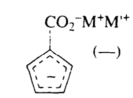
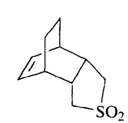
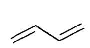
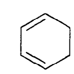
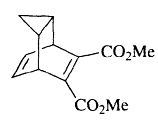
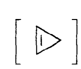
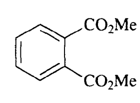
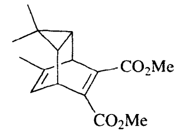
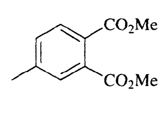
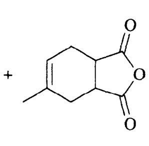
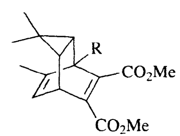
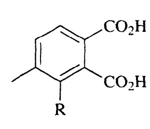
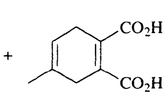
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 650°	 + CP R[1] / R[2] / (%) CO_2Et / H / 80 CO_2Et / n-C_5H_{11} / 80 COMe / n-Bu / 56 CONHBu-*i* / H / 67 $CON(CH_2)_5$ / n-C_5H_{11} / 75 CONHBu-*i* / n-C_5H_{11} / 90 CONHBu-*i* / I / 75  I	755
 Ar = *p*-anisyl	180°	 (87) + CP + COS	756
 *exo*[d]	≥400°	 + CP + $C_{10}H_{14}$ ("*ca.* equal amounts")[e]	173, 757
	FVP, 270 - 500°	 (—) & isomers	758
	200°	 R / (%) / ee(%) Me / 90 / >98 n-Bu / 90 / >98	759
	200 - 220°	 (—) +  * (≥ 98 ee)	760
	(—) $M^+,M'^+ = Li^+,K^+$	 (—) +  (—)	236
	FVP, 750°	 (—) +  (60) + C_6H_6 (20)	750
	240°, 1 h	 +  (—)	761
 + MA	180 - 200°	 (—) +  (65)	762
 + DMAD R = H or Me	1. vacuum distill 2. hydrolysis	 (—) +  (—)	762

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

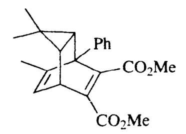
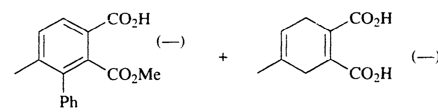
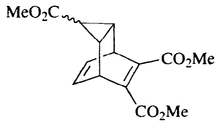
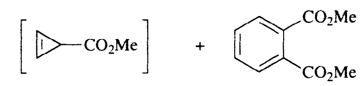
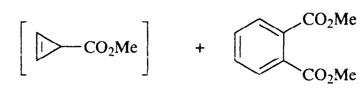
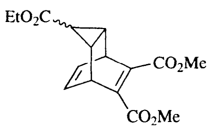
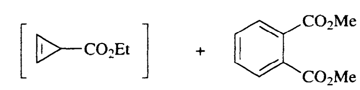
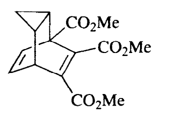
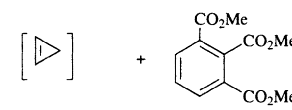
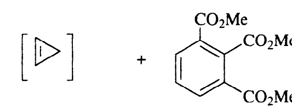
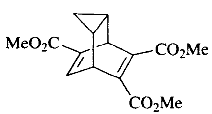
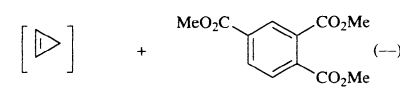
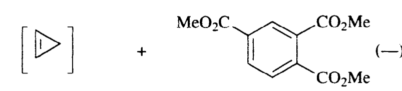
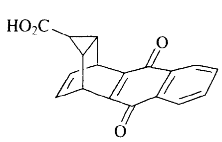
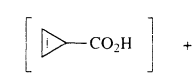
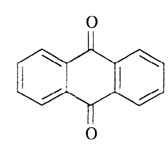
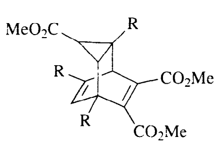
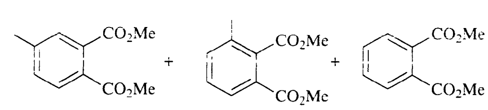
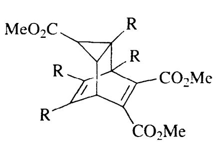
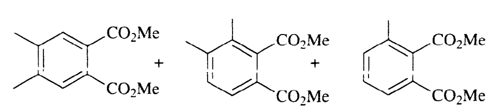
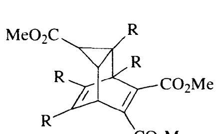
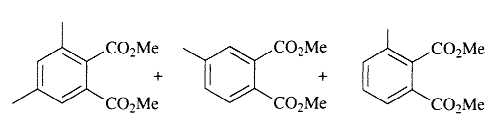
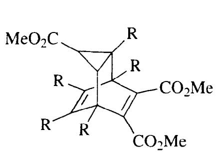
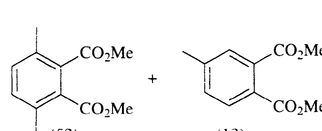
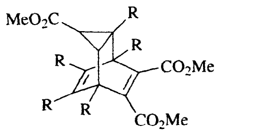
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	1. 200° 2. hydrolysis	 (—) + (—)	762
	pyrolysis	 (—)	763
	200 - 300°	 (—)	764
	250°	 (—)	765
	250°	 (—)	765
	200 - 300°	 (—)	764
	250°	 (—)	765
	200 - 300°	 (—)	764
	220°	 dienophile not analyzed +  (—)	765
 mixture: R = mono-Me, others H	260 - 280°	 (38) + (22) + (3)	268a
 mixture: R = *vic* di-Me, others H	260 - 280°	 (32) + (32) + (16)	268a
 mixture: R = 1,3 di-Me, others H	260 - 280°	 (28) + (21) + (21)	268a
 mixture: R = 1,4 di-Me, others H	260 - 280°	 (52) + (13)	268a

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.

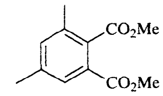
Starting Material:



mixture: 1,3,5-tri-Me, others H

Conditions: 260 - 280°

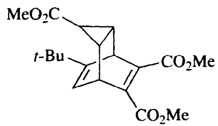
Product(s) and Yield(s) (%):



(85)

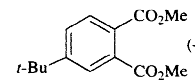
Refs.: 268a

Starting Material:



Conditions: 300°

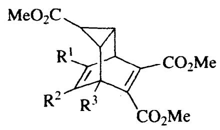
Product(s) and Yield(s) (%):



(—)

Refs.: 268a

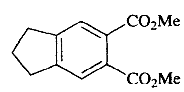
Starting Material:



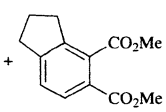
R^1	R^2	R^3
—$(CH_2)_3$—		H
H	—$(CH_2)_3$—	

Conditions: 260 - 280°

Product(s) and Yield(s) (%):



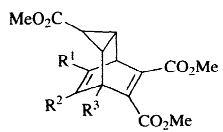
(—) +



(—)

Refs.: 268a

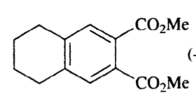
Starting Material:



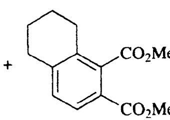
R^1	R^2	R^3
—$(CH_2)_4$—		H
H	—$(CH_2)_4$—	

Conditions: 260 - 280°

Product(s) and Yield(s) (%):



(—) +

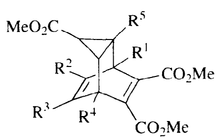


(—)

ca. 1:1

Refs.: 268a

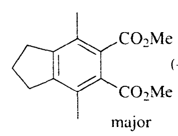
Starting Material:



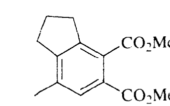
R^1	R^2	R^3	R^4	R^5
Me	—$(CH_2)_3$—		Me	H
—$(CH_2)_3$—		Me	H	Me

Conditions: 260 - 280°

Product(s) and Yield(s) (%):



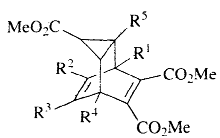
(—) major +



(—) minor

Refs.: 268a

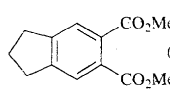
Starting Material:



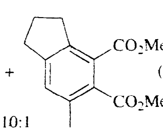
R^1	R^2	R^3	R^4	R^5
H	—$(CH_2)_3$—		H	Me
—$(CH_2)_3$—		H	Me	H

Conditions: 260 - 280°

Product(s) and Yield(s) (%):



(—) +

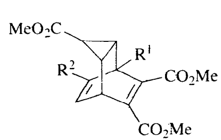


(—)

ca. 10:1

Refs.: 268a

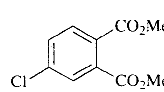
Starting Material:



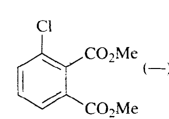
R^1	R^2
Cl	H
H	Cl

Conditions: 280 - 300°

Product(s) and Yield(s) (%):



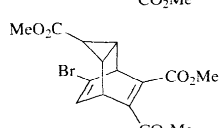
(—) +



(—)

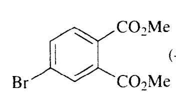
Refs.: 268a

Starting Material:



Conditions: 280°

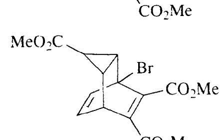
Product(s) and Yield(s) (%):



(—)

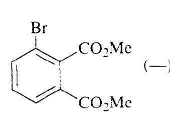
Refs.: 268a

Starting Material:



Conditions: 280°

Product(s) and Yield(s) (%):



(—)

Refs.: 268a

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

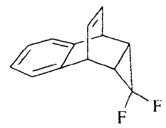
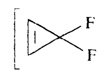
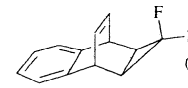
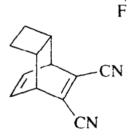
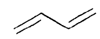
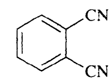
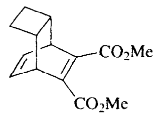
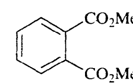
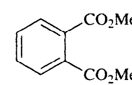
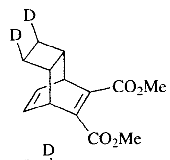
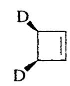
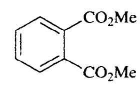
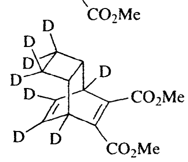
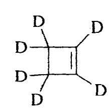
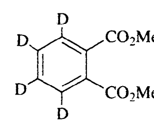
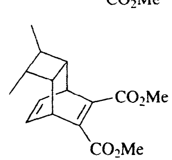
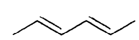
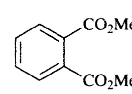
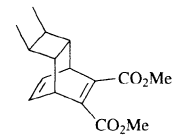
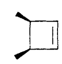
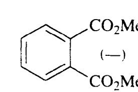
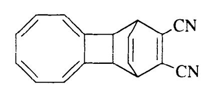
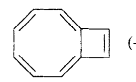
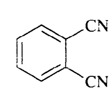
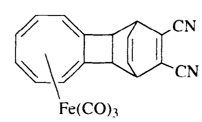
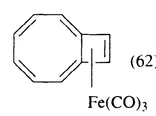
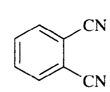
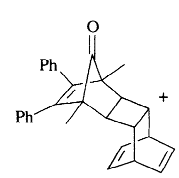
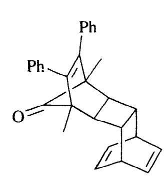
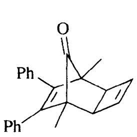
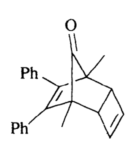
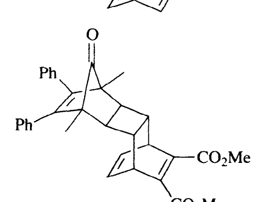
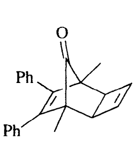
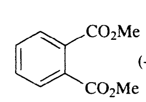
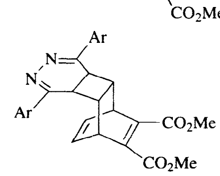
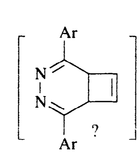
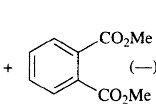
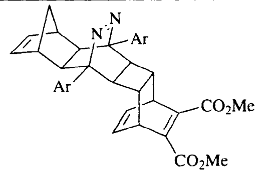
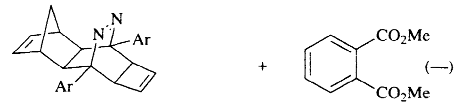
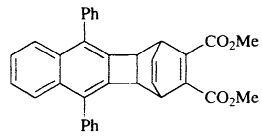
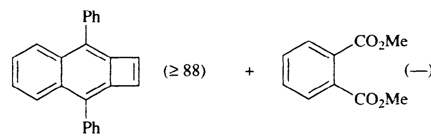
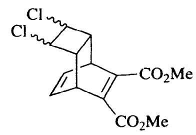
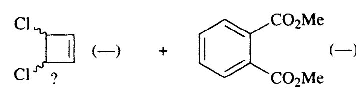
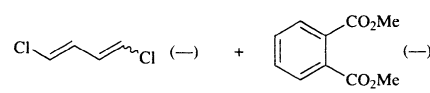
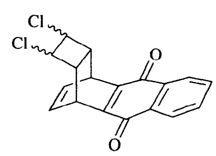
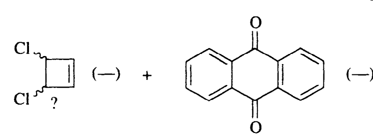
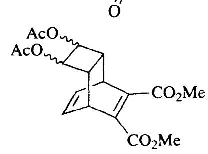
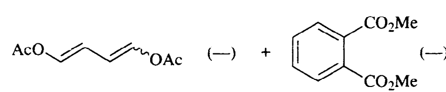
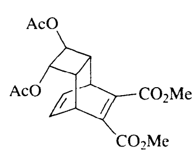
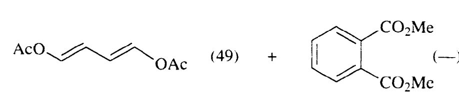
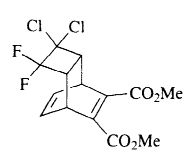
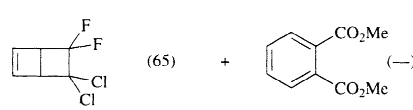
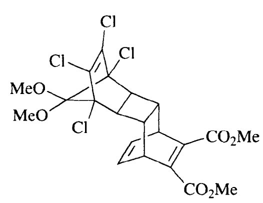
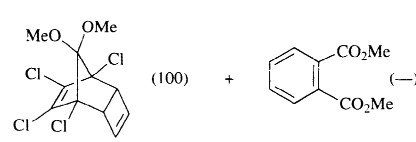
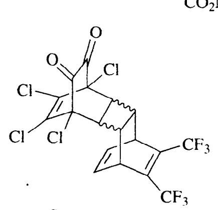
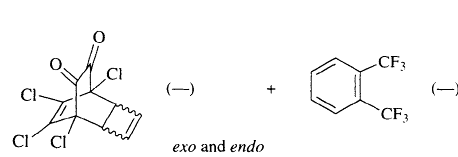
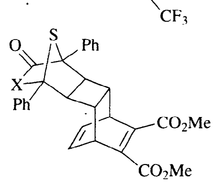
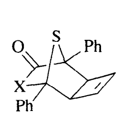
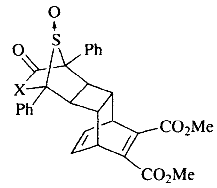
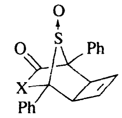
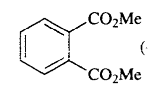
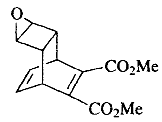
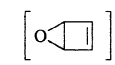
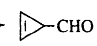
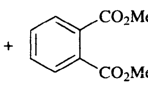
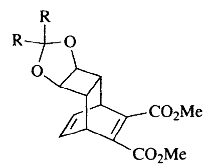
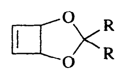
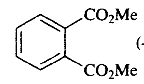
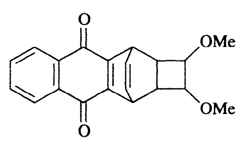
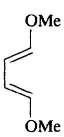
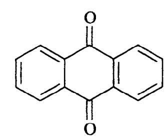
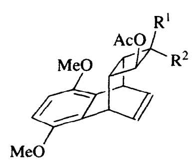
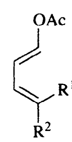
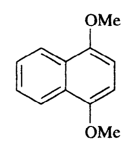
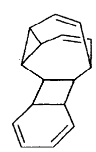
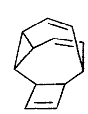
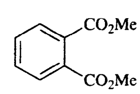
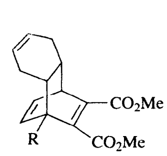
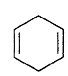
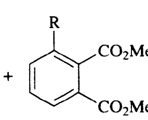
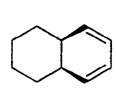
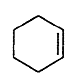
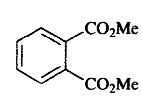
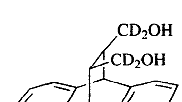
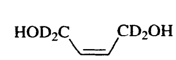
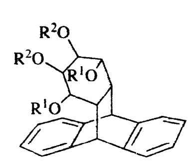
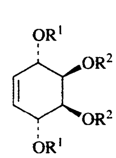
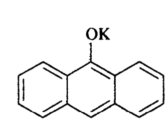
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	200°	 +  (—) + naphthalene	766, 167,168
	185°, sealed tube, 40 h	 (—) +  (97)	767
	200°	 (39) +  (—)	768
	200°, N_2	 (95) +  (—)	769
	200°	 (—) +  (—)	770
	200°, 100 Torr	 (—) +  (—)	771
	200°	 *E,E* (57) +  (—)	349
	200°	 (68) + hexadienes (22) +  (—)	349
	240°, GLC	 (—) +  (—)	772
	180°	 (62) +  (—)	772
 + 	160°	 (—) +  (—) + benzene	279
	180°	 (—) +  (—)	773
	140°	 Ar / $t_{1/2}$ (h) (%): Ph 3.5 —; 2-pyridyl 2 — +  (—)	774, 775

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	130°	 (—) Ar / $t_{1/2}$ (h) / (%) 2-pyridyl / 14 / 85 Ph / — / 40	774, 775
	heat	 (≥ 88) + (—)	776
	220 - 240°	 (—) + (—)	371
	150°, 70 Torr	 (—) + (—)	777
	190°	 (—) + (—)	371
	180 - 220°	 (—) + (—)	777
	170 - 200°, vacuum distill	 (49) + (—)	778
	150 - 160°	 (65) + (—)	779
	200°	 (100) + (—)	780
	210°	 (—) + (—) *exo* and *endo*	781
	heat	 X / Temp / (%) S / 138° / 80 NPh / 182° / 56 + (—)	782

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	138°	 X (%): S 79; NPh 70 +  (—)	782
	FVP, 420 - 540°	 "Dewar furan" →  (99 - 1) → furan (1 - 90) +  (10 - 100)	351
	180°	 R (%): H —; Me 40 +  (—)	783
	170°	 (82) +  (—)	784
	320 - 340°	 (75 - 90) R^1 R^2: D H; H D +  (—)	350
 + DMAD	160°	 (—) +  (—)	785
	*ca.* rt to 100°	 (—) +  (—)	228
 + DMAD	80°	 (—) +  (—)	786
	300 - 350°	 (75) + Anth	339
 R^1 R^2: Me Me; H H; CH_2OBn *i*-Pr	KH, 25°, 2 h	 (—) + 	226

(Ref. 228 data:)

R	Temp	$t_{1/2}$ (min)	E_a (kcal/mol)
H	100°	236	29.0
OTMS	60°	176	26.0
O^-	rt	rapid	20

160

161

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

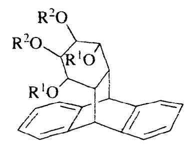
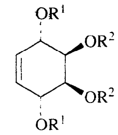
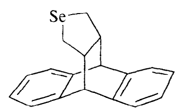
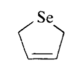
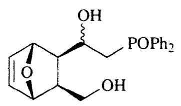
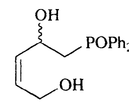
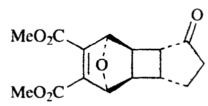
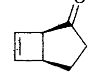
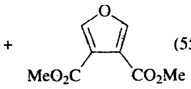
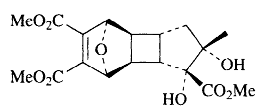
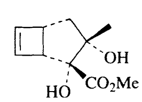
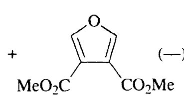
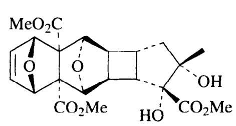
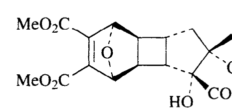
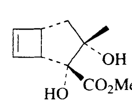
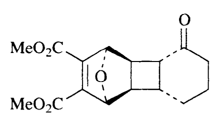
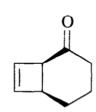
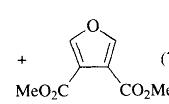
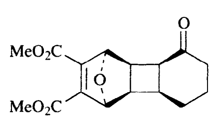
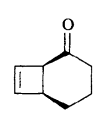
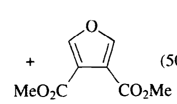
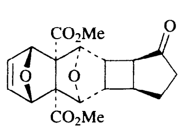
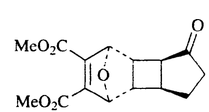
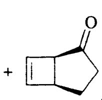
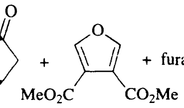
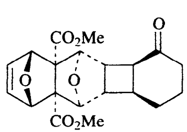
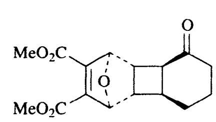
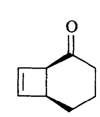
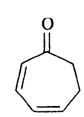
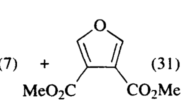
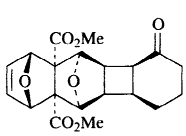
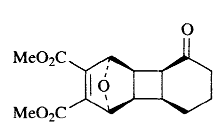
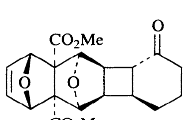
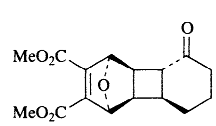
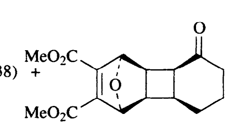
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 460°	 R¹ R² (%): H H 100; Me Me —; Me H — + $C_{10}H_{14}$ (—)	226
	FVP, 540°	 (25) + $C_{10}H_{14}$ (—)	788
	150°, 10 min	 (83) + furan (—)	789
	140°	 (52) +  (55)	790
	220°	 (63) +  (—)	790
	140°	 (67) +  (7)	790
	300 - 330°	 (44) +  (78)	790
	300 - 330°	 (45) +  (50)	790
	140°	 (60) +  (12) +  (20) + furan	790
	140°	 (65) +  (13) +  (7) +  (31) + furan	790
	140°	 (61) + furan	790
	140°	 **I** (38) +  **II** (44) + furan; **I** —220°→ **II** (100)	790

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

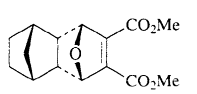
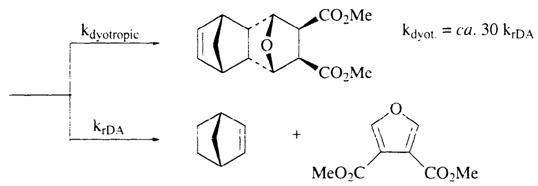
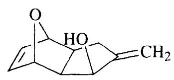
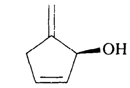
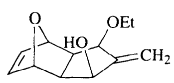
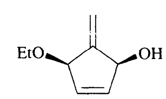
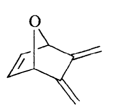
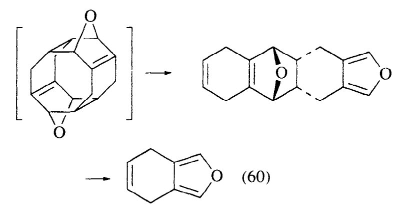
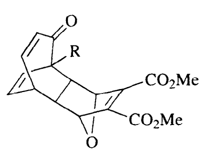
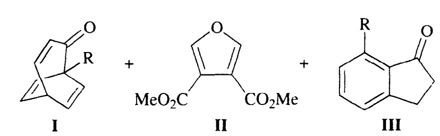
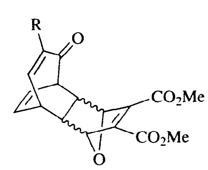
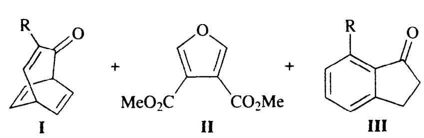
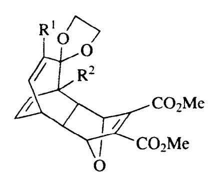
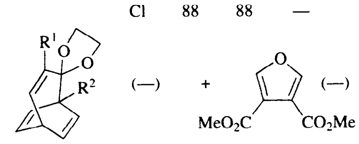
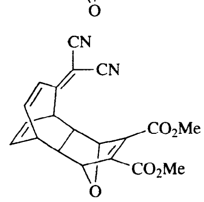
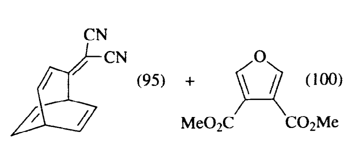
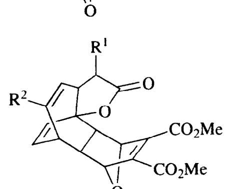
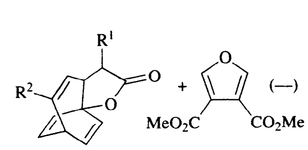
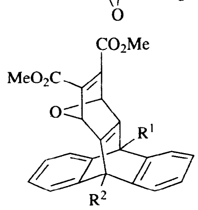
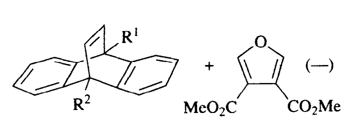
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	130°	 $k_{dyot.} = ca.\ 30\ k_{rDA}$	791
	FVP, 400°	 (100) + furan	792
	FVP, 400°	 (100) + furan	792
	150°, 12 h	 (60)	395
	120 - 130°	 I + II + III R / I (%) / II (%) / III (%) H / 26 / 48 / 22 OH / 39 / 81 / 36 OMe / — / 100 / 95 Cl / 17 / 62 / 17	793, 794
	120 - 130°	 I + II + III R / I (%) / II (%) / III (%) OMe / 50 / 60 / — Cl / 88 / 88 / —	793, 794
 R^1, R^2 = H, Cl isomers	heat	 (—) + (—)	795
	130°	 (95) + (100)	796, 797
	130°	 (—) R^1 / R^2 / (%) H / H / 54 CO_2Me / CO_2Me / 57 CO_2Me / Cl / 70 CO_2Me / OMe / 55	796, 797
	210°	 (—) R^1 / R^2 / (%) Br / H / 87 CN / H / 86 Br / Br / 89	798, 799

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

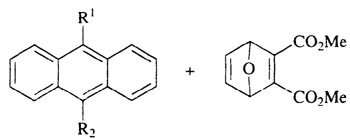
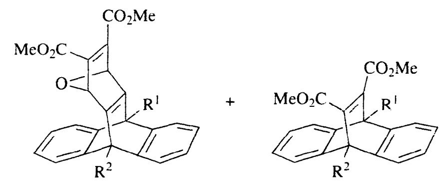
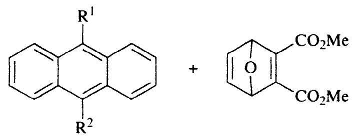
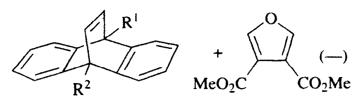
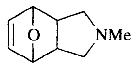
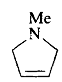
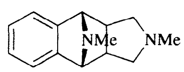
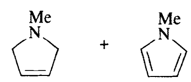
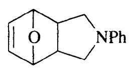
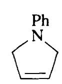
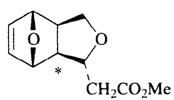
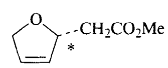
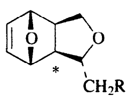
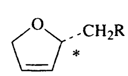
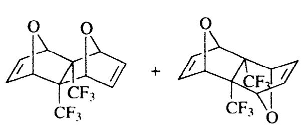
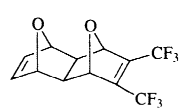
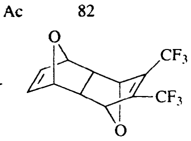
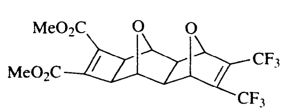
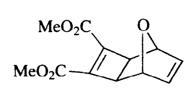
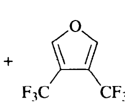
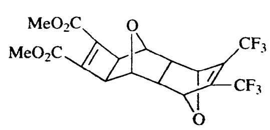
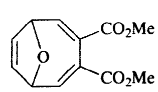
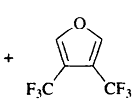
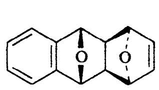
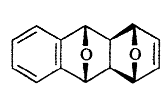
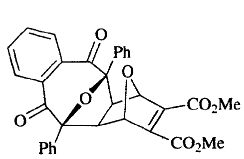
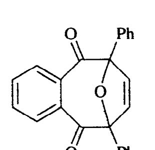
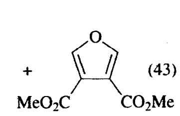
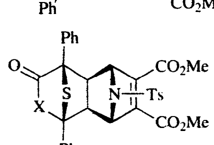
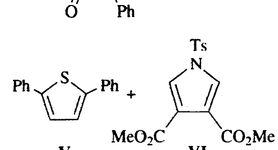
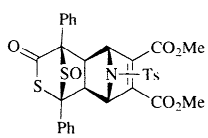
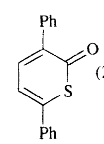
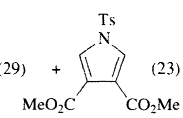
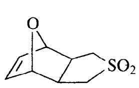
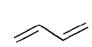
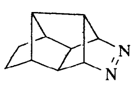
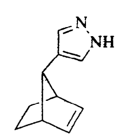
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140°, DMSO	 I + II R¹ / R² / I/II / I (%) Br / H / 76/23 / — CN / H / 93/7 / — Br / Br / — / 82	798, 799
	1. 140°, 2 d 2. 210°	 (—) R¹ / R² / (%) Br / H / 75 CN / H / 75 Br / Br / 76 Me / H / 51 Me / Me / 67	798, 799
	250 - 300°, silicone oil	 (60) + furan	747
	240°	 III + IV / III (%) / IV (%) *endo* / 76 / 9 *exo* / 54 / 36	220
	250 - 300°, 60 Torr	 (83) + furan	747
	FVP, 500°	 (85) + furan	800
	FVP, 500°	 + furan R / (%) / ee (%) CO_2Me / 90 / 94 CN / 83 / Ac / 82 /	801
	120°	 (20) +  (38)	802
	FVP, 490°	 (90) +  (—)	802, 739
	FVP, 550°	 (—) +  (—)	802
	160°, 8 h	 (20)	803
	140°	 (86) +  (43)	804
	heat	 V + VI + [OCX] X / Temp / V (%) / VI (%) S / 80° / 67 / 64 NPh / 112° / 88 / 82	805

TABLE V. 1,2-DIALKYLETHYLENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat	 (29) +  (23) + [SO]	805
	FVP, 675°	 (51) + furan (72)	750
	380°, flow	 (95)	806

[a] Starting material was recovered ≤ 0.2% rearranged.

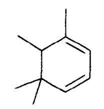
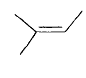
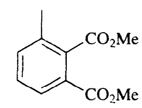
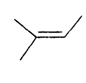
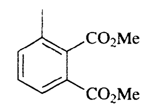
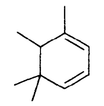
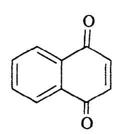
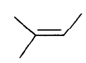
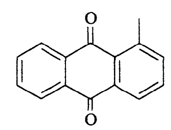
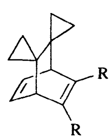
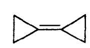
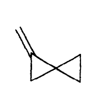
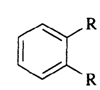
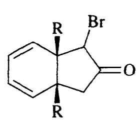
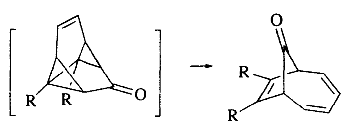
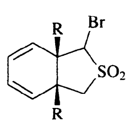
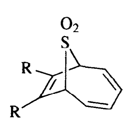
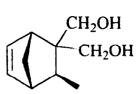
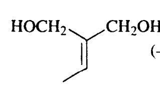
[b] This reaction proceeds either by a retro[2 + 2] or [3 + 3] followed by a second rDA.

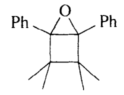
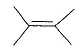
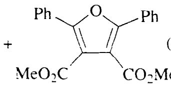
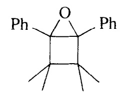
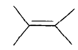
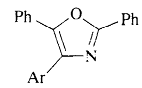
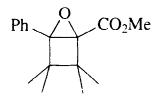
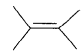
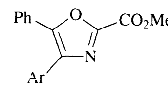
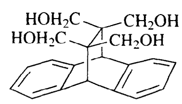
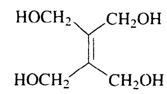
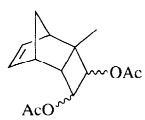
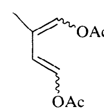
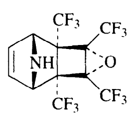
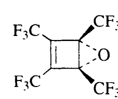
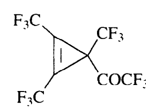
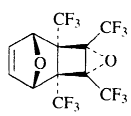
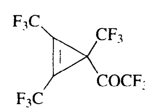
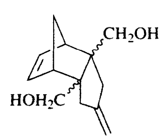
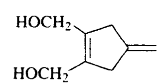
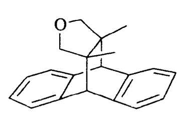
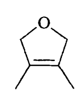
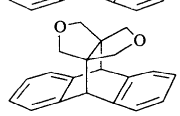
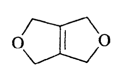
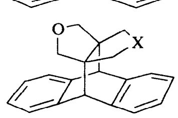
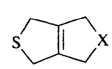
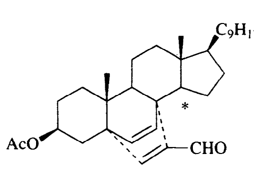
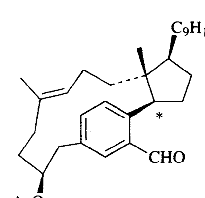
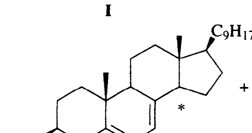
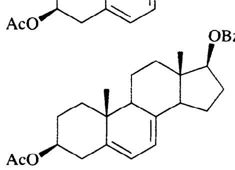
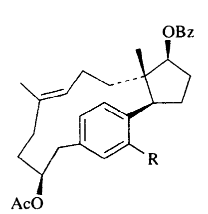
[c] **I** and **II** are more reactive than **III.** At higher reaction temperatures, product **V** was formed in higher yield than product **IV**. UV irradiation of **V** gave a mixture of *endo* and *exo* **IV**.

[d] The *endo* isomer is stable to 400°.

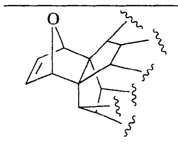
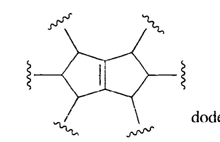
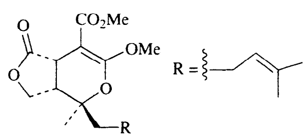
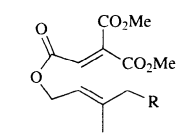
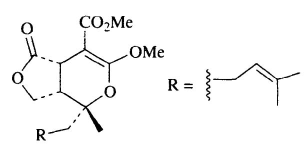
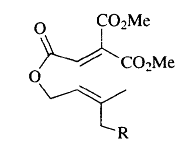
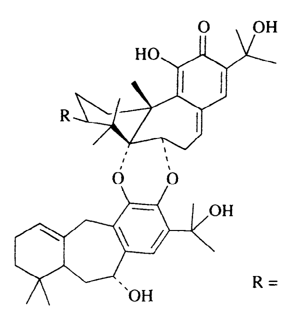
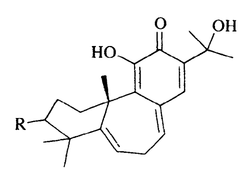
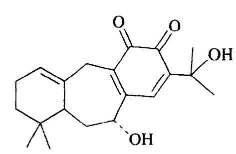
[e] *Cf.* 9-aza analogue (ref. 757).

TABLE VI. TRI- AND TETRAALKYLETHYLENES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD α-pyronene	heat	 [a] (—) +  (—)	712, 713
	120 - 150°	 (—) +  (—)	641
 + 	heat (oxid.)	 (—) +  (—)	712, 713
 R = CO_2Me or CN	FVP, 525°	 +  +  (—) 5 : 95 (94)	355
	KOBu-*t*, DMSO, rt	 R,R (%): Me, Me 16; $-(CH_2)_4-$ —	252, 253
	KOBu-*t*, DMSO, rt	 R,R (%): Me, Me 27; $-(CH_2)_4-$ 56; $-(CH_2)_5-$ 58	253, 254
	520°	 (—) + CP (—)	807

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	120°	 (—) +  (—)	356
 + ArCN Ar = Ph, *p*-tolyl	120°	 (—) +  (—)	356
 + PhCN	120°	 (—) +  ("good")	357
	300°	 (75) + $C_{10}H_{14}$ (—)	352
	FVP, 460°	 (—) + CP (—)	735
	85°, PTAD[b]	 (55) —95°→  (—)	272
	200°	 (—) + furan (—)	272
	FVP, 575°	 (—) + CP (—)	808
	FVP, 550°	 (100) + $C_{10}H_{14}$ (—)	352, 353
	FVP, 600°	 (100) + $C_{10}H_{14}$ (—)	352,353
 X = O or S	FVP, 700°	 (100) + $C_{10}H_{14}$ (—)	354
 **I**	112°	 (100) **II**	359
 + ≡—CHO	112°	[**I**][c] → **II** (85)	358
 + ≡—R	1. 0°, BF_3 2. 140°		360

R	(%)
CHO	100
Ac	"high"
CO_2Me	"less satisfactory"
CN	"less satisfactory"

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	550°	 (>90) + furan (—) dodecahedrene	809
	heat, ⇌	 (—)	810
	heat, ⇌	 (—)	810
 R = H or OAc	61°	 (—) +  (—)	811

[a] The structure of this product was proven by bromination.

[b] PTAD is a scavenger for pyrrole.

[c] I can be isolated by carrying out the reaction as a Lewis acid catalyzed DA reaction at a lower temperature.

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS

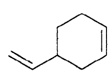
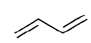
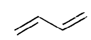
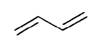
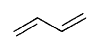
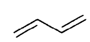
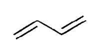
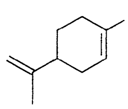
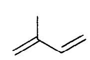
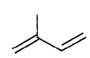
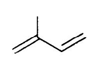
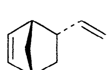
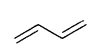
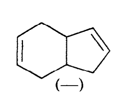
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	627 - 777°, shaker tube E_a = 62.0 log A = 15.2	 (—)	333
	E_a = 61.8	 (—)	812
	510 - 704°, flow E_a = 71.3	 (—)	813
	235 - 292° $\Delta H^{\#}$ = 54.3 $\Delta S^{\#}$ = 4	 (—)	363
	700°	 (80)	576
	pulsed laser, 1025 cm^{-1} SiF_4	 (—)	513
	700°	 (81)	576, 9, 13
	pulsed laser	 ("major")	814
	pulsed laser, 1025 cm^{-1} SiF_4	 (—)	513
 *endo*	235 - 292°	 (—) + CP (—) +  (—) | | $\Delta H^{\#}$ | $\Delta S^{\#}$ | rDA 34.6 −6 Cope 32.7 −6	363

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

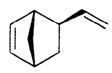
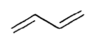
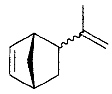
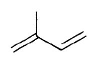
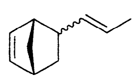
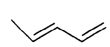
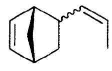
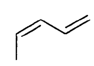
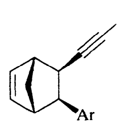
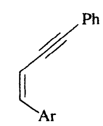
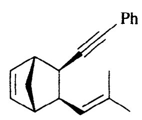
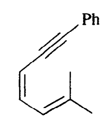
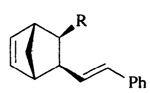
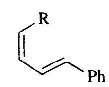
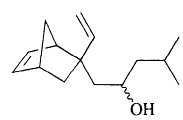
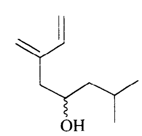
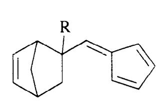
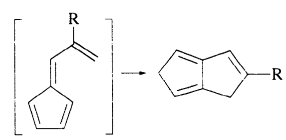
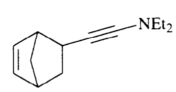
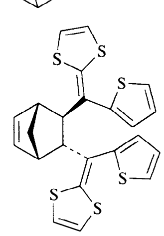
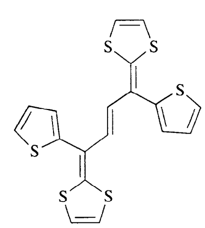
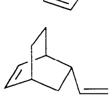
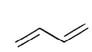
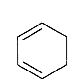
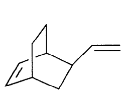
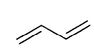
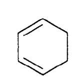
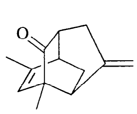
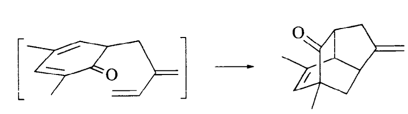
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 *exo*	235 - 292°	 (—) + CP (—) | | ΔH# | ΔS# | | rDA | 32.4 | −10 |	363
 *endo* + *exo*	235 - 292°	 (—) + CP (—) | | ΔH# | ΔS# | | *endo* rDA | 35.4 | 1 | | Cope | 36.1 | 3 | | *exo* rDA | 35.1 | −6 |	363
 *endo* + *exo*	235 - 292°	 (—) + CP (—) | | ΔH# | ΔS# | | *endo* rDA | 39.1 | 5 | | Cope | 32.7 | −6 | | *exo* rDA | 41.7 | 7 |	363
 *endo* + *exo*	235 - 292°	 (—) + CP (—) | | ΔH# | ΔS# | | *endo* rDA | 41.0 | 7 | | Cope | nd | nd | | *exo* rDA | 39.0 | 3 |	363
 Ar = Ph, *p*-(Me, Cl, CN, or OMe)	200°	 (73 - 89) + CP (—)	815
	200°	 (77) + CP (—)	815
	200°	 | R | (%) | | ≡—Ph | 70 | | Ph | 83 | | vinyl | 69 | | $H_2C{=}C(OEt)$ | 56 | + CP (—)	815
	FVP, 450°	 (100) (+/−)-ipsenol + CP (—)	156
	FVP, 520°	 | R | (%) | | H | 58 | | Me | 41 | + CP (—)	816
	FVP, 500°	 (100) + CP (—)	685
	180°	 (73) + CP (—)	817
	203 - 290°, gas phase $E_a = 51.6$ log A = 14.46	 (—) +  (—)	362
	240 - 305°, gas phase $E_a = 53.0$ log A = 14.95	 (—) +  (—)	362
	176°, $t_{1/2}$ = 42 h	 (—)	818

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

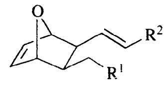
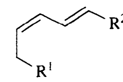
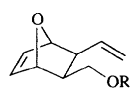
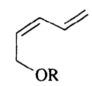
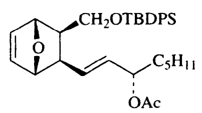
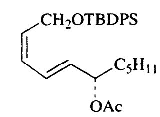
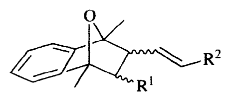
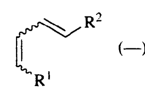
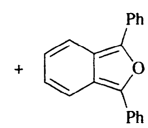
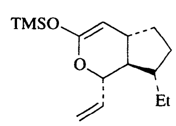
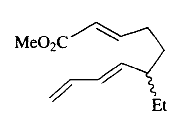
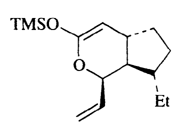
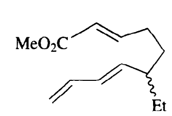
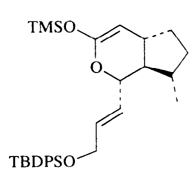
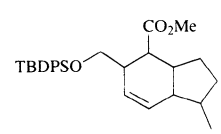
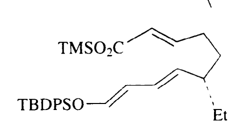
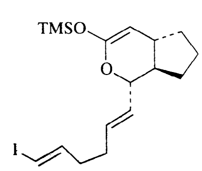
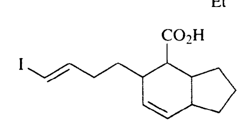
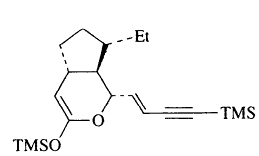
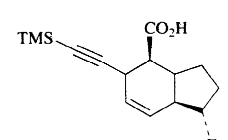
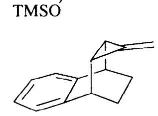
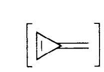
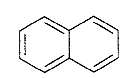
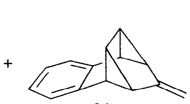
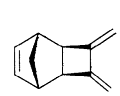
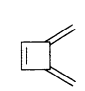
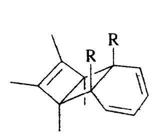
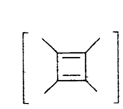
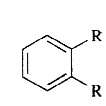
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140°	 + furan R[1] / R[2] / (%) OTHP / R'CHOTBDMS / 85 (R' = undefined alkyl) OTBDMS / OTHP / >61 OTHP / CHO / 87	819
 R = 3,5-dinitrobenzoyl-	170°, 5 min	 (90) + furan (—)	789
	130°, 3 h	 (85) + furan (—)	820
 R[1] = Me, Ph, or CO_2Me R[2] = Ph or CO_2Me	heat, or UV	 (—) +  (—)	821
	1. 100°, 5 h 2. CH_2N_2	 (53)	822
	1. 135°, 20 h 2. CH_2N_2	 (42)	822
	1. 135°, 24 h 2. CH_2N_2	 (72)	822
	105°	 (72)	823
	140°, 12 h	 (71)	824
	140°, 12 h	 (66)	823
	> 400°	 +  (minor) +  (36)	825
	425°	 (—) + CP (—)	826
 R / R CO_2Me / CO_2Me CH_2OH / CH_2OH —C(O)CH_2C(O)— —CH_2OCH_2—	UV, rt; or UV, −196°; or heat	 +  (—)	373

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

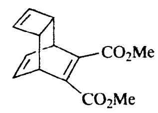
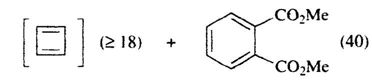
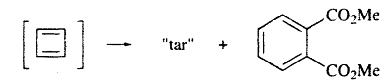
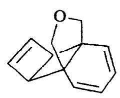
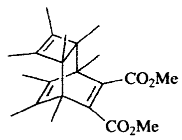
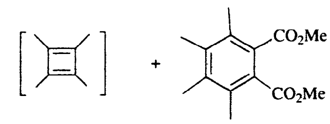
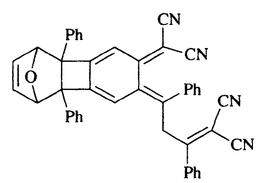
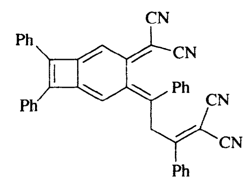
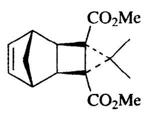
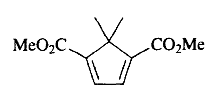
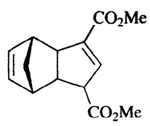
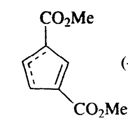
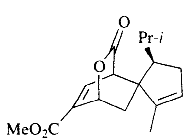
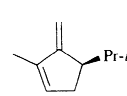
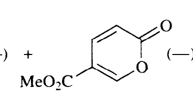
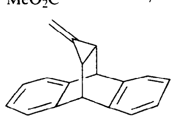
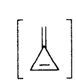
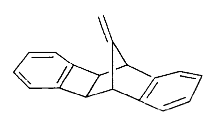
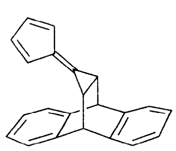
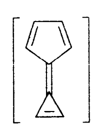
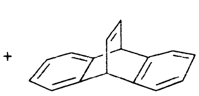
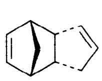
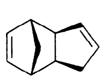
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV	 (≥ 18) + (40)	372
	heat	 → "tar" + (—)	371, 65
	UV	 + (—)	827
	330 - 350°	 + (—)	828
	161°, 5 h	 (71) + furan (—)	829
	160°	 (91) + CP (—)	830
	550°	 (—) + CP (—)	830
	110° ⇌ 50°	 (—) +  (—)	831
	FVP, 500°	 + $C_{14}H_{10}$ (4) +  (56)	832, 833
	FVP, 900°	 + $C_{14}H_{10}$ (—) +  (—)	834, 833
	152 - 211° $\Delta H^{\#} = 33.0$; $\Delta S^{\#} = -1.9$	CP (—)	366, 365, 20
	200 - 352° $\Delta H^{\#} = 37.4$; $\Delta S^{\#} = 1.1$	CP (—)	366, 365
$(CP)_2$ (presumably mainly *endo*)	heat, neat liq.; $E_a = 34.3$	CP (—)	835
	155 - 222° $E_a = 33.7$; log A = 13	CP (—)	836
	135 -175°; paraffin $E_a = 34$	CP (—)	837, 259
	100 - 155°; $E_a = 35.4$	CP (—)	838, 259, 839
	Differential Thermal Analysis $E_a = 36.1$	CP (—)	840
	160°	CP (87)	841
	Flow pyrolysis, 350 - 400°	CP (91)	842

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

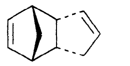
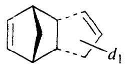
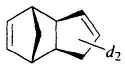
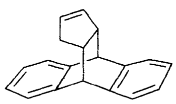
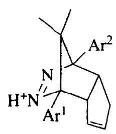
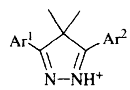
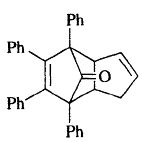
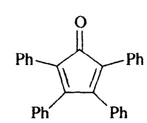
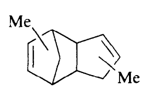
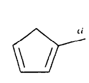
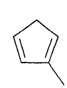
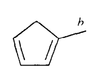
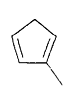
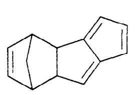
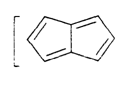
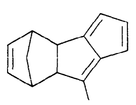
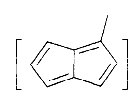
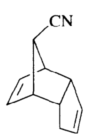
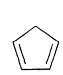
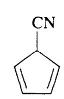
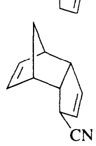
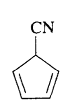
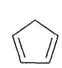
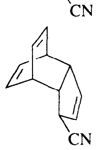
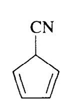
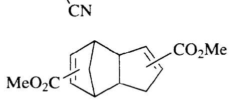
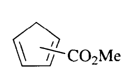
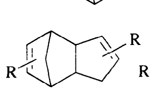
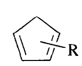
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	In liquid crystal: smectic mesophase; 180 - 194° nematic mesophase; 205 - 219°	CP (—)	843
	196°	$(CP)_2$ (—) + $(CP)_2$-d_1 (—) + $(CP)_2$-d_2 (—)	844
	196°	$(CP)_2$ (—) + $(CP)_2$-d_2 (—) + $(CP)_2$-d_4 (—)	844
	214 - 246° E_a = 40.8; log A = 14.1	CP (—) + $C_{10}H_{14}$ (—)	169
	TFA, 20° ⇌	CP (—) +  (—) Ar[1] / Ar[2] / K_{eq}: p-OMe / p-OMe / 200 p-Me / p-Me / 26 H / H / 11 p-F / p-F / 8.3 p-Cl / p-Cl / 5 p-Br / p-Br / 3.1 m-CN / m-CN / 0.32 p-NO_2 / p-NO_2 / 0.24 p-NO_2 / p-OMe / 6.3 p-CO_2Me / p-Me / 4.6	196
 mp 188 - 190° (dec.)	attempts to recrystallize ⇌	CP (—) +  (—)	440
	≥ 172°	 [a] (—) +  (—)	845
	heat	 [b] (—) +  (—)	846
	200°	CP (—) +  → [2 + 2] dimers (—)	376
	FVP, 600 - 650°	CP (—) +  [c] (30)	375, 374
	rt, LTMP (2 equiv)	 (—) +  (—)	244
	rt, LTMP (2 equiv)	 (—) +  (—)	244
	rt, LTMP (1 equiv)	 (—) + benzene (—)	244
	heat (distill) ⇌ rt	 (—)	377
 R = CO_2Me, CN or COCl	150°	 (—)	847

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

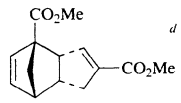
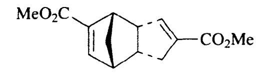
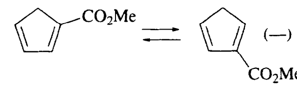
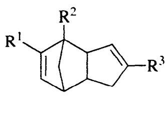
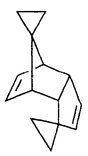
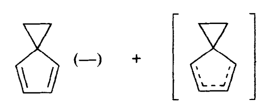
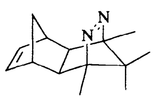
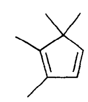
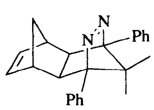
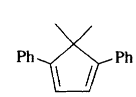
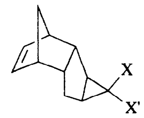
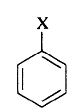
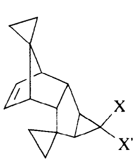
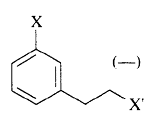
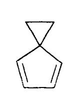
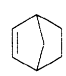
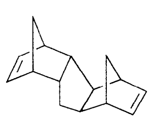
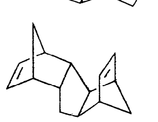
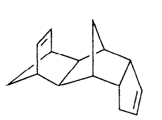
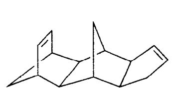
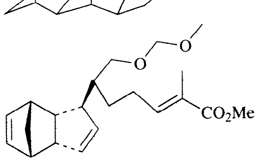
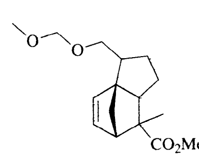
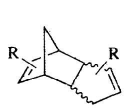
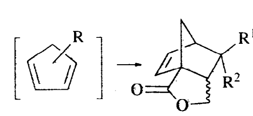
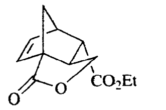
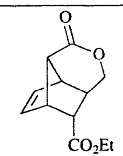
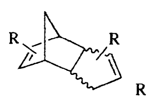
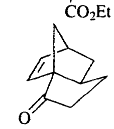
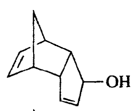
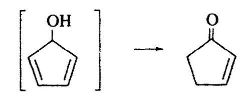
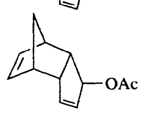
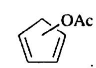
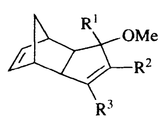
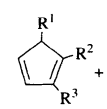
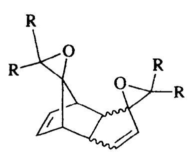
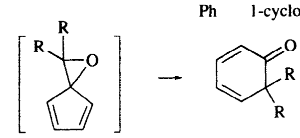
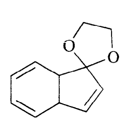
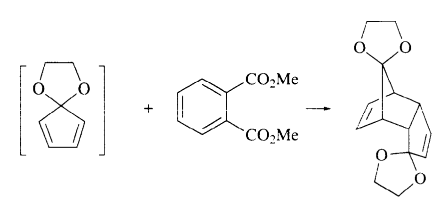
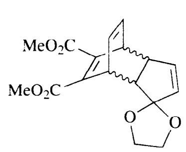
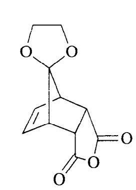
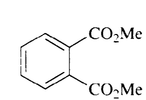
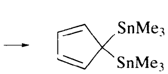
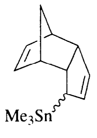
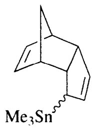
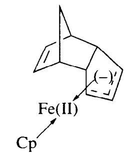
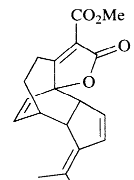
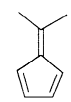
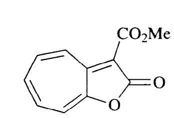
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 I [d]	heat (⇌)	 II (—)	378
I and/or II	101 - 140° $\Delta H^{\#} = 25.9$; $\Delta S^{\#} = -13.3$	 (—)	378
	heat	 (—) R¹ / R² / R³ / E_a / $\Delta S^{\#}$: H / H / H / 35.1 / 1.1 H / H / CO_2Me / 32.2 / 0.7 CO_2Me / H? / CO_2Me / 30.4 / 1 mix Me, H / — / Me / 37.1 / 4.3 H? / *t*-Bu / *t*-Bu / 27.1 / −3.5	379
	? (+ e⁻)	 (—) + [ ]$^{\cdot +}$	848[e]
	photoelectron transfer −1 e⁻	 (2 - 3) + CP (—)	849
	photoelectron transfer −1 e⁻	 (12 - 47) + CP (—)	849
 X, X' = Cl or Br	200°	 (—) + CP (—) + HX'	850
 X, X' = Cl or Br	200°	 (—) +  (—)	850
$(CP)_2$ + C_2H_4	230°	 (80)	364
	k (300°) = 2.4 x 10^2 s^{-1} $\Delta H^{\#} = 29.4$; $\Delta S^{\#} = -15.6$	CP (—)	851
	k (300°) = 2.6 x 10^2 s^{-1} $\Delta H^{\#} = 30.7$; $\Delta S^{\#} = -13.2$	CP (—)	851
	k (300°) = 2.4 x 10^2 s^{-1} $\Delta H^{\#} = 28.1$; $\Delta S^{\#} = -17.7$	CP (—)	851
	k (300°) =1.3 x 10^2 s^{-1} $\Delta H^{\#} = 31.6$; $\Delta S^{\#} = -12.9$	CP (—)	851
	180°	 (83) + CP (—) 1 : 1 mixture of diastereomers	852
 R = CO_2CH_2CH=CHR¹R²	200°	 R¹ / R² / (%): H / H / 76 *exo* Me / Me / 20 *exo/endo* = 10 H / CO_2Et / 67 equil. mix	853

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	K_{eq} = 2.6 ⇌	 (—)	853
 R = $COCH_2CH_2CH{=}CH_2$	200°	 (30) exo only	853
	450°	 (42) + CP (—)	380
	440 - 475°	 (—) + CP (—) mixture	380
	1. K, BuLi, THF, rt 2. H_2O	 + CP (—) mixture (see table below)	247
	400°	 (see table below)	237
 + DMAD	160°	 (72)	854
 + MA	160°	 (79) +  (—)	384
$(CP)_2$	*n*-BuLi, KOBu-*t*, Me_3SnCl	[CP + Cp] →  (9)	243
	MeLi, −78°	[CP + Cp] → Cp (—) + $(CP)_2$ (—)	246
	$FeCl_2$, MeLi, −78°	 (20)	246
	138°	 (—) +  (60)	385

Ref. 247 products:

R^1	R^2	R^3	(%)
Ph	Ph	Ph	90
Me	Ph	Me	63
Bu	Ph	Ph	86
Me	Ph	Ph	76
Ph	Bu	H	91
Ph	$MeO(CH_2)_3$	H	68
Ph	$MeO(CH_2)_3$	H	95
Ph	$CH_2{=}CH(CH_2)_2$	H	65
Ph	1-cyclohexenyl	H	62

Ref. 237 products:

R,R	(%)
Me,Me	40
$-(CH_2)_5-$	—

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

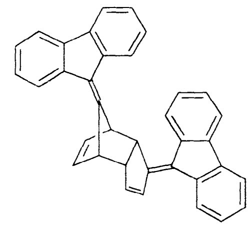
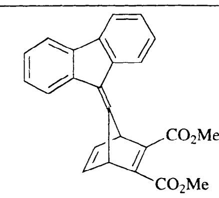
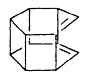
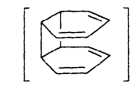
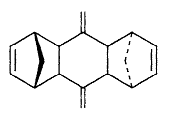
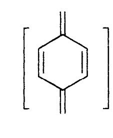
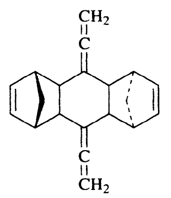
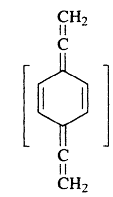
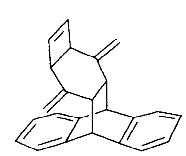
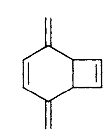
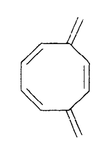
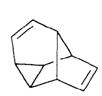
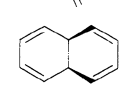
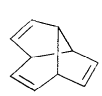
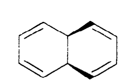
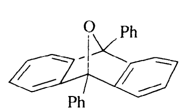
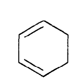
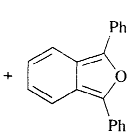
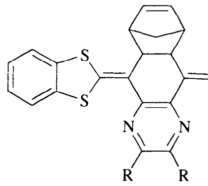
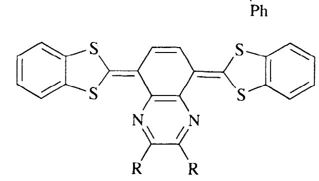
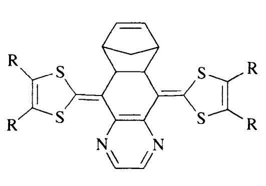
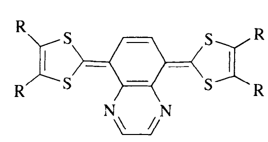
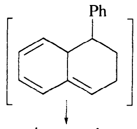
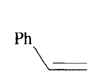
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + DMAD	180°	 (50)	855
 C_2 symmetry	160 - 185° $\Delta H^{\#} = 36.0$; $\Delta S^{\#} = 3.1$	 → benzene (—)	856
	FVP, 680°	 + CP (—)	857
	FVP, 680°	 + CP (—)	857
	FVP, 310°	 (19) + $C_{14}H_{10}$ (38)	858
	450°	 (77) + $C_{14}H_{10}$ (—)	858
	120 -130°	 (50)	859, 860
	280°	 (—)	860
	heat, or UV	 (—) +  (—)	821
 R = H, Me, or Ph	200°	 (100) + CP (—)	861
	—	 (100) + CP (—) R, R: H, H; Me, Me; benzo; —$S(CH_2)_4S$—	862
 various products	UV ⇌	 (—)	863

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

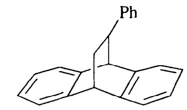
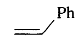
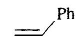
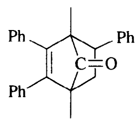
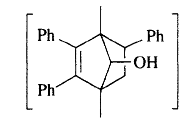
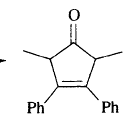
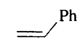
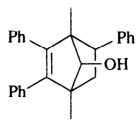
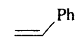
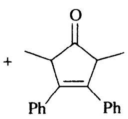
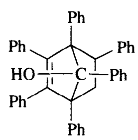
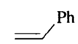
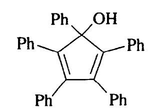
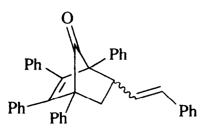
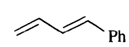
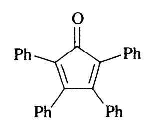
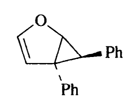
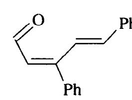
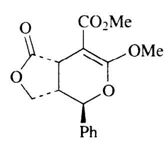
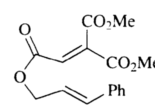
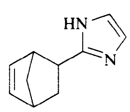
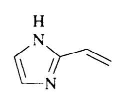
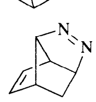
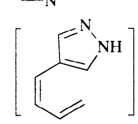
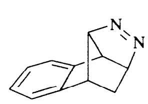
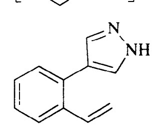
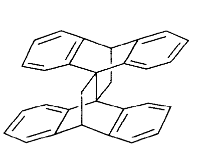
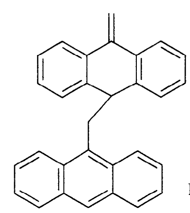
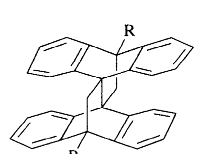
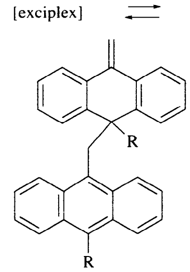
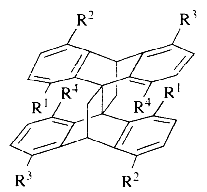
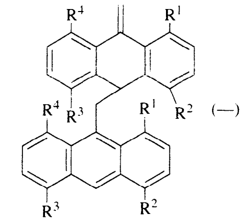
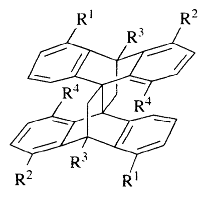
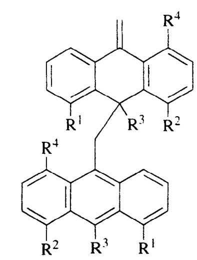
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	250°, Ph_2O $k = 1.45 \times 10^{-3} s^{-1}$	 (—) + $C_{14}H_{10}$ (—)	175, 176
	UV	 (—) + $C_{14}H_{10}$ (—) + $(C_{14}H_{10})_2$ (60)	864
	KOH, EtOH	 →  ("principal") +  (—)	381
	distill, 1 atm.	 (—) +  (—)	381
	300°, 15 Torr	 (35) +  (—)	865
	≥ 110° ⇄ 80°	 (—) +  (—)	866
	heat, or UV, or H^+	 (—)	204
	K_{eq} (85°) = 2; (115°) = 8 ⇄ $\Delta H° = 14.3$; $\Delta S° = 41$	 (—)	810
	500°	 (—) + CP (—)	867
	FVP, 350°	 (95)	868
	FVP, 400°	 (100)	869, 870
 I	K_{eq} ⇄ K_{eq} (21°) = 1.23×10^{-3} K_{eq} (49°) = 3.88×10^{-3} $\Delta H° = 7.6$; $\Delta S° = 12.7$	 II (—)	386
	UV ⇄	[exciplex] ⇄ II ⇄ I	388, 390
	— K_{eq} (25°) 1.6×10^{-3} 10^{-7} 5×10^{-7} 3×10^{-6} 5×10^{-5}	 (—) R / K_{eq} (25°) H / 1.6×10^{-3} Me / $\leq 10^{-7}$ Et / $\leq 5 \times 10^{-7}$ Br / 3×10^{-6} Ph / 5×10^{-5}	386

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	25° (⇌)	 (—)	387

R^1	R^2	R^3	R^4	K_{eq}
Cl	H	H	H	1.6×10^{-2}
Cl	H	Cl	H	1.3×10^{-3}
Cl	H	H	Cl	3×10^{-5}

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	⇌	 (—)	388

R^1	R^2	R^3	R^4	K_{eq} (25°)
H	H	H	H	1.45×10^{-3}
Cl	H	H	Cl	0.33×10^{-3}
H	Cl	H	H	15.9×10^{-3}
H	Cl	H	Cl	1.27×10^{-3}
H	Cl	Me	H	10^{-7}
H	Cl	Et	H	10^{-6}
H	Cl	*n*-Bu	H	10^{-6}
H	Cl	Ph	H	5×10^{-5}
H	Cl	1-naphthyl—CH_2—	H	10^{-6}
H	Cl	2-styryl	H	10^{-6}

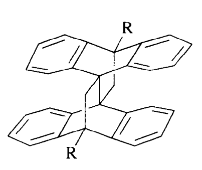
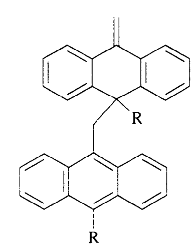
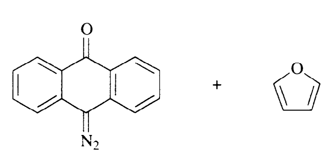
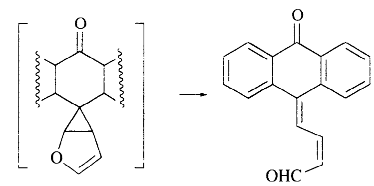
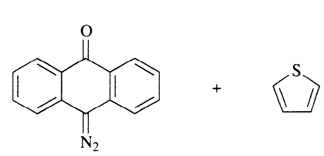
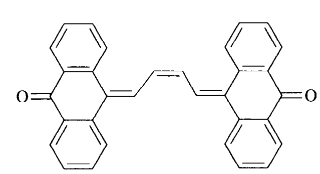
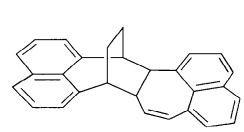
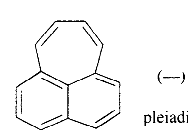
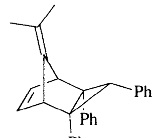
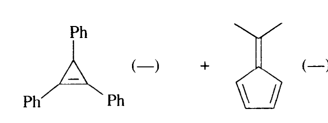
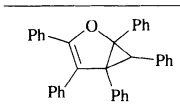
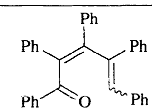
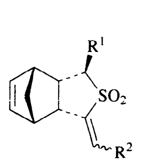
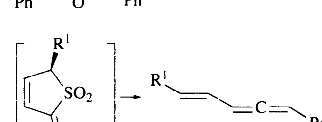
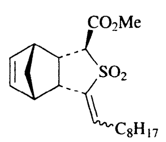
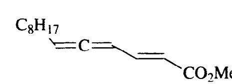
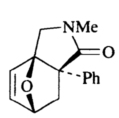
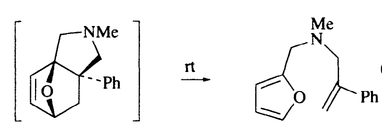
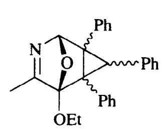
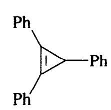
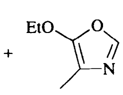
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	270 - 320°, (>mp)	 (—)	389
	UV	 (44)	871
	UV	 (30)	872
	UV, 313 nm	 (—) pleiadiene	873
	200°		874

TABLE VII. ARYL- AND VINYL-SUBSTITUTED OLEFINS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	≥ 180°, or UV ⇌ UV	 (64)	875
	FVP, 650°	 + CP (—) R^1 R^2 (%): H Et 78; Me Et 83; H *n*-Bu 86	754
	FVP, 600°	 (25) + CP	755
	LiAlH$_4$	 (100)	876
	"pyrolysis"	 (—) +  (—)	877

[a] The products were separated by GC.
[b] GC-MS was used to evaluate the composition of the dimer.
[c] This compound is isolable at −196°; it dimerizes at −140°.
[d] This is the preferred isomer at low temperature.
[e] This reaction was examined in the DA direction; the rDA reaction is discussed in reference 849.

TABLE VIII. ALLENES AND RELATED POLYENES

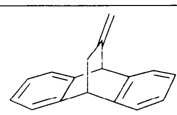
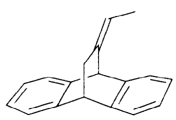
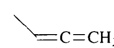
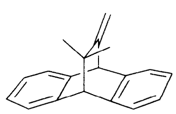
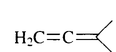
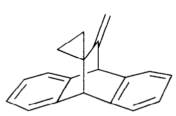
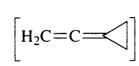
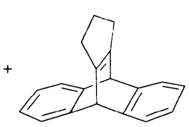
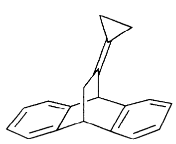
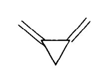
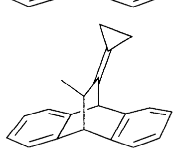
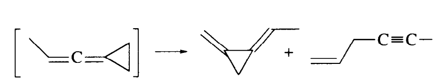
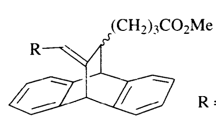
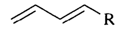
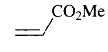
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 800°	$H_2C{=}C{=}CH_2$ (100) + $C_{14}H_{10}$ (—)	393
	FVP, 750°	 (100) + $C_{14}H_{10}$ (—)	393
	FVP, 700°	 (100) + $C_{14}H_{10}$ (—)	393
	FVP, 650°	 I (10) +  (90) + $C_{14}H_{10}$ (—)	337
	FVP, 650°	[I] →  (25) + $C_{14}H_{10}$ (—)	337
	FVP, 650°	 (50) (50) + $C_{14}H_{10}$ (—)	337
 R = H, Me, or $(CH_2)_{10}CH_3$	FVP, 750°	 (—) +  (—) + $C_{14}H_{10}$ (—)	485

TABLE VIII. ALLENES AND RELATED POLYENES (*Continued*)

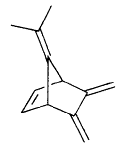
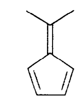
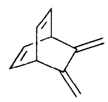
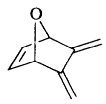
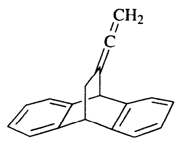
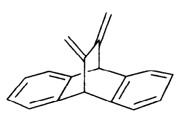
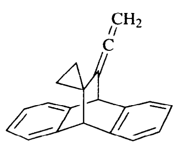
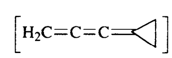
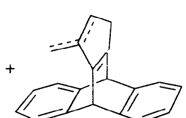
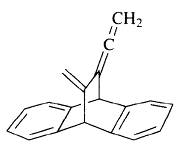
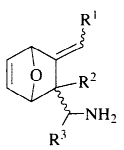
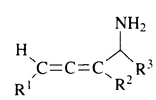
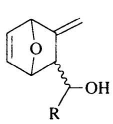
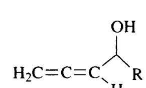
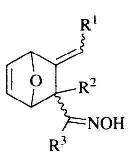
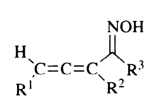
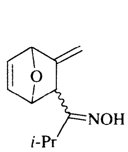
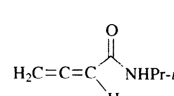
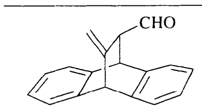
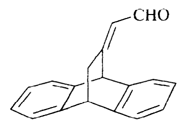
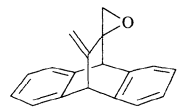
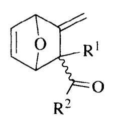
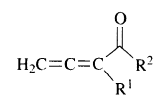
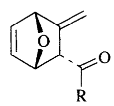
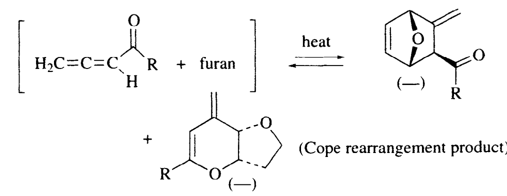
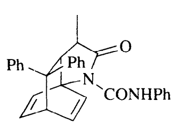
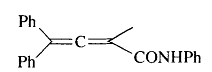
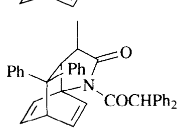
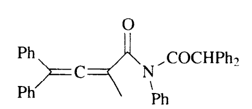
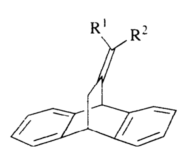
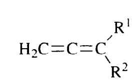
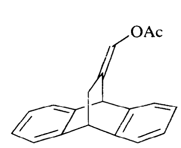
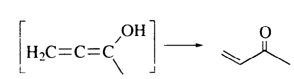
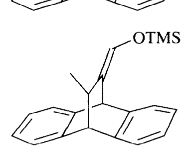
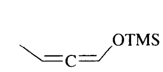
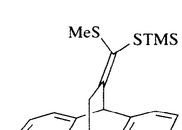
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 500 - 600°	$H_2C{=}C{=}C{=}CH_2$ (2) +  (—)	395
	FVP, 620°	$H_2C{=}C{=}C{=}CH_2$ (100) + C_6H_6 (—)	395
	FVP, 580°	$H_2C{=}C{=}C{=}CH_2$ (80) + furan (—)	395
	FVP, 750°	$H_2C{=}C{=}C{=}CH_2$ (99) + $C_{14}H_{10}$ (—)	393
	FVP, 850°	$H_2C{=}C{=}C{=}CH_2$ (98) + $C_{14}H_{10}$ (—)	393
	FVP, 650°	 (10) +  (90) + $C_{14}H_{10}$ (—)	337
	FVP, 700°	$H_2C{=}C{=}C{=}C{=}CH_2$ (70) + $C_{14}H_{10}$ (—) polymerizes at rt	393, 394
	FVP, 460°	 + furan (—) R¹ R² R³ (%) H H *n*-Pr 67 H Me Me 78 H H *i*-Pr 63 H H Me 65 H H Et 70 H H Ph 75 Et Et Me 74	878, 879
	FVP, 480 - 510°	 + furan (—) R (%) Me 71 Et 70 *i*-Pr 72 (Me)₂ 70	878, 879
	FVP, 450 - 510°	 + furan (—) R¹ R² R³ (%) H H Et 71 H H *n*-Pr 75 H Me Et 65 H H Ph 62 H Me Me 73 Et H Me 67 *n*-Pr H Ph 52 H H Me 74 MOM H Ph 80	878, 879
	FVP, 450°	 (68) + furan (—)	878

TABLE VIII. ALLENES AND RELATED POLYENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 700°	$H_2C{=}C{=}CHCHO$ (25) + $C_{14}H_{10}$ (—)	485, 484
	FVP, 700°	$H_2C{=}C{=}CHCHO$ (50) + $C_{14}H_{10}$ (—)	485, 484
	FVP, 750°	$H_2C{=}C{=}CHCHO$ (30) + $C_{14}H_{10}$ (—)	485, 484
	FVP, 450 - 480°	 R^1 R^2 (%) H *i*-Pr — SPh Et 72 Me Ph 98 + furan (—)	878, 879
 R = Et, *n*-Pr, or *i*-Pr	heat ⇌		880
	135°	 (—) + PhNCO (—)	397
	K_{eq} (80°) = 0.25 ⇌	 (—)	223
	FVP, 575°	 R^1 R^2 (%) H OTMS 60 Me OTMS 65 CN CN 50[a] CN CO_2Et 20 CN CO_2Me 55 CO_2Et CO_2Et 20 CO_2Me CO_2Me 50 + $C_{14}H_{10}$ (—)	485, 881
	FVP, 600 - 900°	 (—) + CO + $C_{14}H_{10}$ (—)	485
	FVP, 575°	 (60) + $C_{14}H_{10}$ (—)	485
	FVP, 660°	[$H_2C{=}C{=}C{=}S$] (≥ 25) + $C_{14}H_{10}$ (100) + MeSTMS	882, 509, 331

[a] This product polymerizes at 0°.

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS

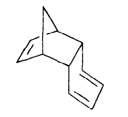
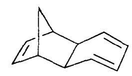
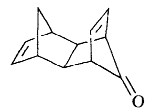
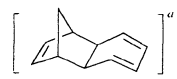
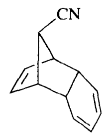
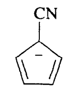
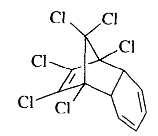
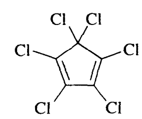
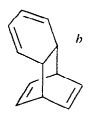
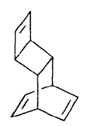
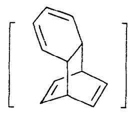
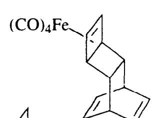
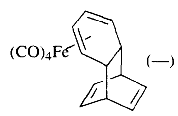
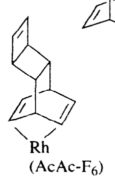
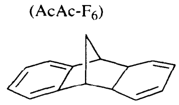
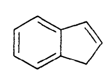
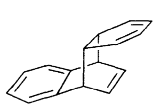
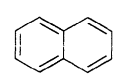
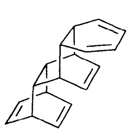
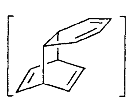
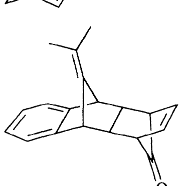
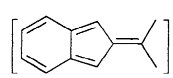
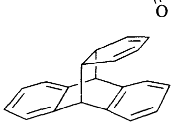
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	≤ 60°	C_6H_6 (—) + CP (—)	883
	42 - 60° $\Delta H^{\#} = 27.5$; $\Delta S^{\#} = 8.2$	C_6H_6 (—) + CP (—)	174, 280
	39 - 60° $\Delta H^{\#} = 24.9$; $\Delta S^{\#} = 3.5$	C_6H_6 (—) + CP (—)	174, 280
	60°	 [a] → C_6H_6 (—) + CP (—)	883
	rt, LTMP (1 equiv)	C_6H_6 (—) +  (—)	244
	135°, 23 h	C_6H_6 (—) +  (—)	174
 [b]	−68 to −52° $\Delta H^{\#} = 14.3$; $\Delta S^{\#} = -6$	C_6H_6 (—)	276
	110° $k = 2.24 \times 10^{-5}\ s^{-1}$	 → C_6H_6 (—)	884
	100°, 1 h	 (—) $\xrightarrow{Ce^{IV}}$ C_6H_6 (—)	884
	110°	C_6H_6 (—)	884
	170°; $t_{1/2}$ = ca. 2 h	C_6H_6 (—) +  (—)	883
	0 - 14° $E_a = 19.55$ log A = 12.07	C_6H_6 (—)  (—)	399
	100° or UV	 + C_6H_6 $\xrightarrow[E_a = 16.5;\ \log A = 13.4]{20 - 55^\circ}$ C_6H_6 (—)	277
	100°	C_6H_6 (—) +  (—) + CO	424
	56 - 80° $E_a = 29.3$ log A = 15.5	C_6H_6 (—) + $C_{10}H_{14}$ (—)	277

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

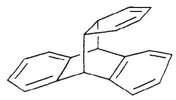
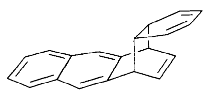
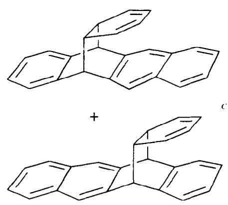
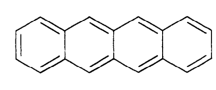
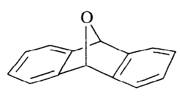
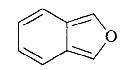
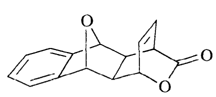
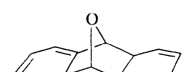
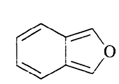
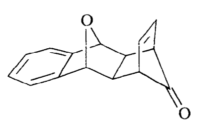
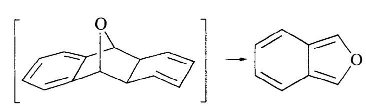
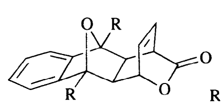
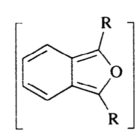
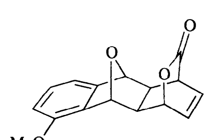
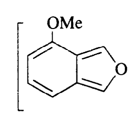
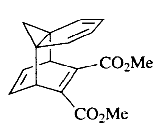
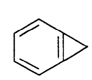
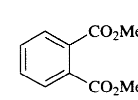
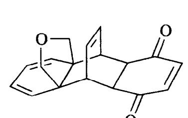
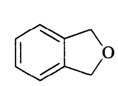
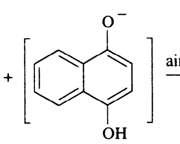
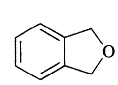
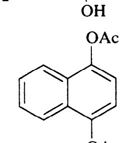
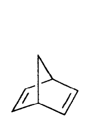
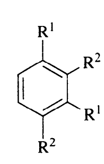
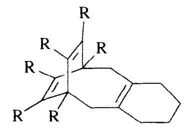
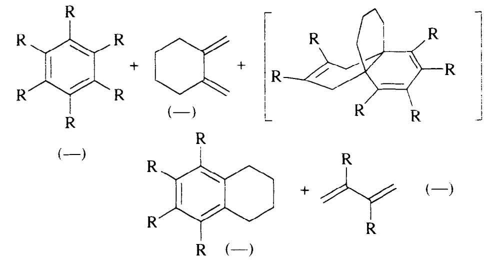
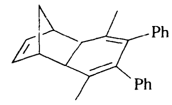
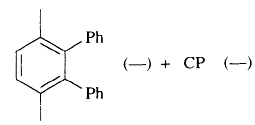
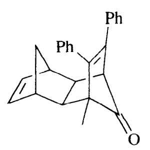
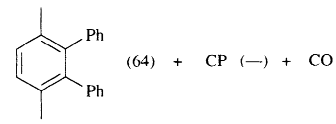
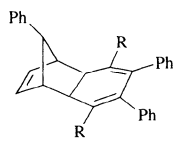
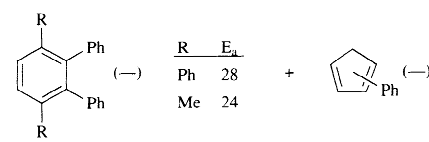
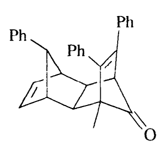
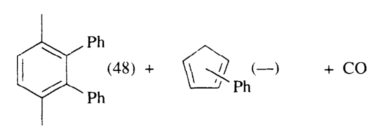
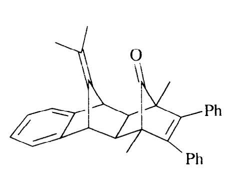
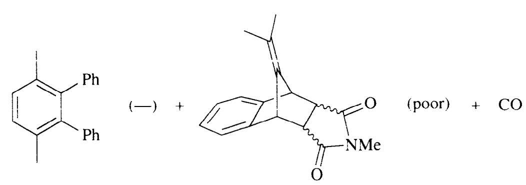
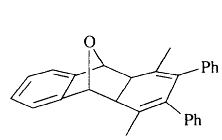
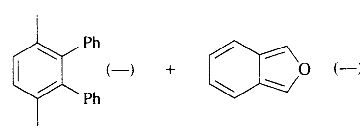
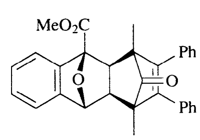
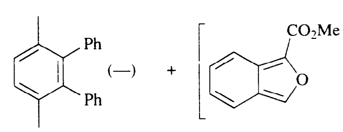
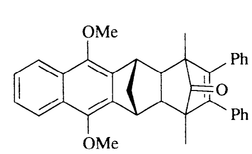
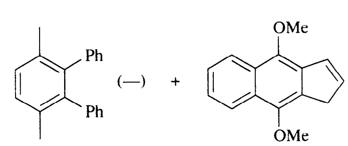
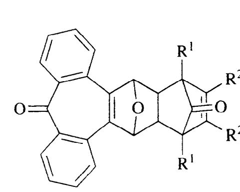
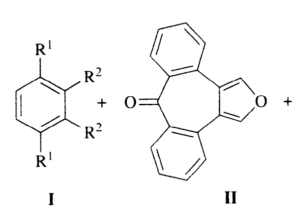
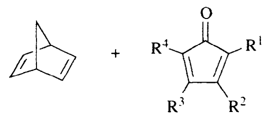
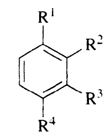
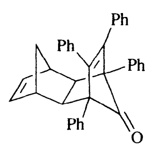
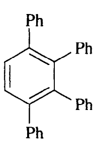
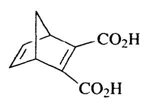
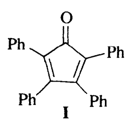
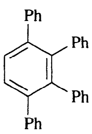
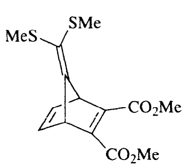
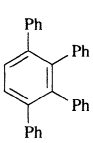
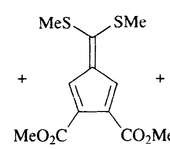
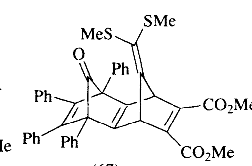
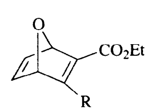
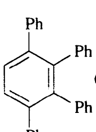
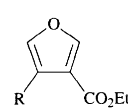
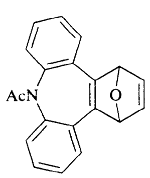
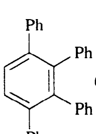
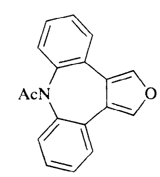
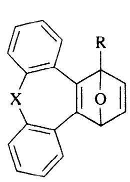
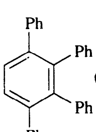
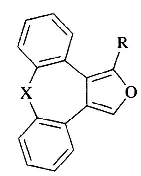
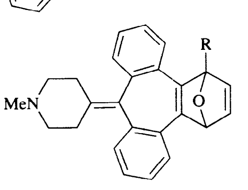
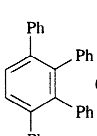
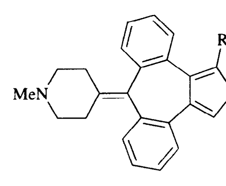
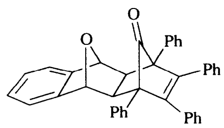
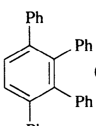
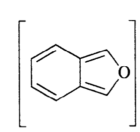
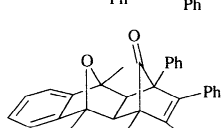
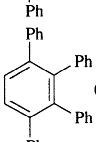
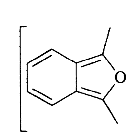
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat $\Delta H^{\#} = 24.3$ $\Delta S^{\#} = -3.0$	C_6H_6 (—) + $C_{10}H_{14}$ (—)	170
	UV	C_6H_6 (—) + $C_{10}H_{14}$ (—) (ground state)	170
	20 - 45° $E_a = 21.8$ log A = 12.3	C_6H_6 (—) + $C_{10}H_{14}$ (—)	277
	80 - 95° $E_a = 30.8$ log A = 14.9	C_6H_6 (—) +  (—)	277
	46.8 - 67° $\Delta H^{\#} = 26.0$ $\Delta S^{\#} = -5.6$ $t_{1/2}$ (46.8°) = 2.4 h	C_6H_6 (—)  (—)	400
	FVP, 130°	 (6) +  (—) + C_6H_6 (—) + CO_2	400
	≥ 110°	 (—) + C_6H_6 (—)	883
 R = H or Me	130 - 150°	C_6H_6 (—) +  (—) + CO_2	408, 885
 mixture of regioisomers	140°	C_6H_6 (—) +  (93) + CO_2	886
	400°, 1 Torr	 (45) +  (—)	404
	NaOMe, rt	 (30) +  naphthoquinone (—)	887
	pyridine, Ac_2O, 85°	 (—) +  (—)	887
 + R^1—≡—R^2 R^1 R^2: Me H; Ph H; Me Me; Ph Ph	20 - 130°, catalyst cat. = $Fe(COT)_2$ *or* $FeCl_3$/*i*-PrMgCl	 (20 - 40) + CP (—)	888

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = H, D	180°	 (—) + (—) + [ ] → (—) + (—) (—)	889
	heat, or UV $t_{1/2}$ (33°) = 19 min	 (—) + CP (—)	401
	112°, 24 h	 (64) + CP (—) + CO	402
	—	 (—) R, E_a: Ph 28; Me 24 + (—)	402
	112°, 24 h	 (48) + (—) + CO	402
 + NMM	215° $t_{1/2}$ = 45 min	 (—) + (poor) + CO	274
	heat, or UV $t_{1/2}$ (33°) = 2-3 d	 (—) + (—)	401
	140°	 (—) + [ ] (—) + CO	890
	pyrolysis	 (—) + (90)	891
	120°	 I + II + CO	892

R^1	R^2	I (%)	II (%)
Ph	Ph	90	70
Me	Ph	39	50
Cl	Cl	95	59

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat	 + CP (—) + CO	893
	112°, 3 d	 (98) + CP (—) + CO	402
 +  I	132°	 (58)	893
 + I	100°	 (—) +  (4) +  (67)	894
 + I	150°	 (—) + 	406
 + I	138°	 (—) +  (41)	895
 + I	138°	 (—) + 	896
 + I	138°	 (—) + 	897
	165°	 (—) +  (—)	408, 885, 898, 899, 900, 901
	165°	 (—) +  (—)	408

Subtable for ref. 893 (first entry):

R^1	R^2	R^3	R^3	Temp	Time	(%)
Ph	Ph	Ph	Ph	60°	48 h	92
Me	Ph	Ph	Me (dimer)	132°	2 h	53
Ph	*p*-PhOMe	*p*-PhOMe	Ph	132°	2 h	"high"
	p-PhNMe$_2$	Ph	Ph	132°	2 h	"high"
p-PhOMe	*p*-PhOMe	*p*-PhOMe	*p*-PhOMe	132°	2 h	"high"
Ph	*p*-PhPh	*p*-PhPh	Ph	132°	2 h	"high"

Subtable for ref. 406:

R	(%)
CF_3	38
C_5F_{11}	55
C_7F_{15}	68

Subtable for ref. 896:

X	R	(%)
CO	H	79
SO_2	H	66
CO	Me	53

Subtable for ref. 897:

R	(%)
H	97
Me	62

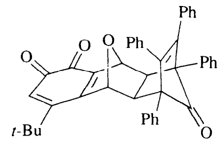
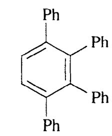
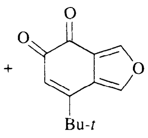
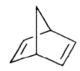
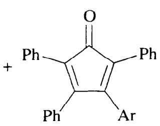
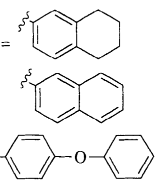
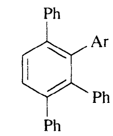
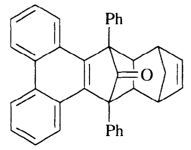
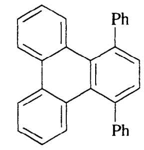
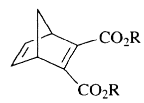
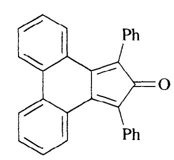
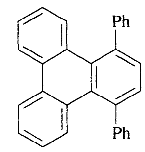
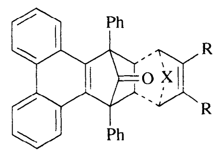
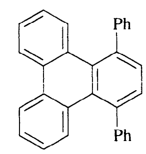
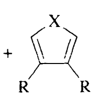
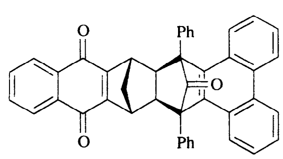
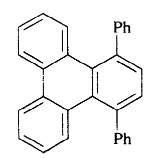
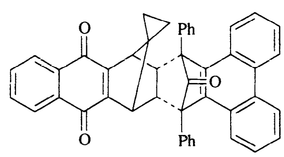
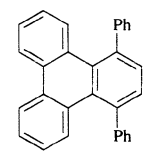
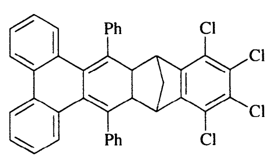
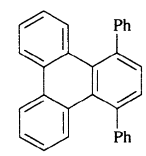
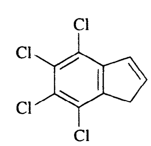
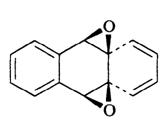
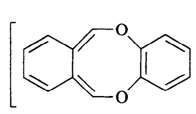
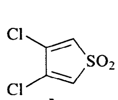
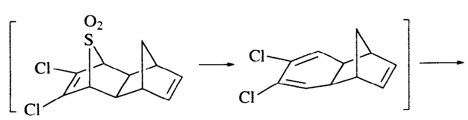
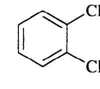
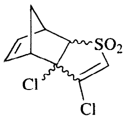
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	130°	 (—) +  (44)	902
 +  Ar = 	132°	 (—) + CP (—)	903
	200°, 0.3 h	 (—) + CP (—)	893
 +  R = H, Me	heat	 (74)	893
	200°	 +  (—) X: O, R,R: CO_2Me, CO_2Me; X: O, R,R: —$(CH_2)_4$—; X: CH_2, R,R: CO_2Me, CO_2Me; X: $C{=}C(Me)_2$, R,R: H,H	904
	230°	 (—)	891
	pyrolysis	 (70)	891
	200°	 (—) +  (30)	893
	k (28°) = 3 x 10^{-5} s^{-1}	 (—)	905
 +  I	61°	  (—) + [CP] [CP] + I ⟶  (28)	906

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

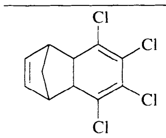
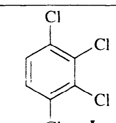
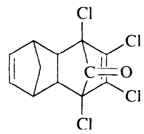
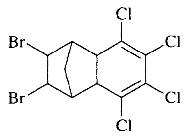
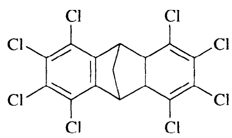
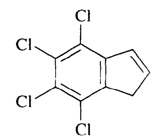
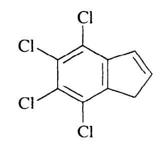
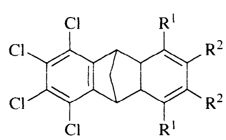
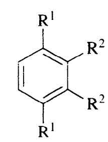
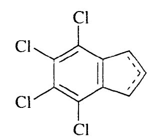
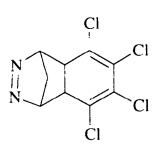
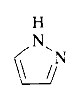
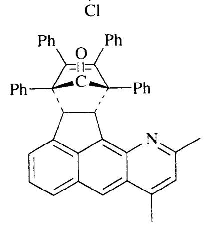
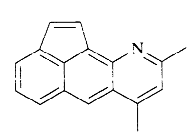
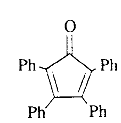
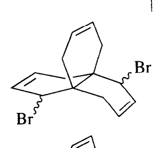
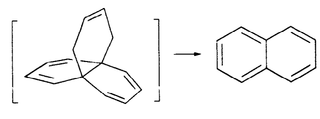
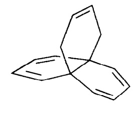
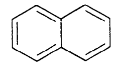
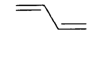
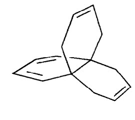
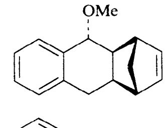
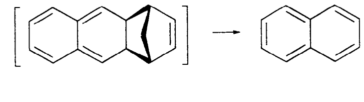
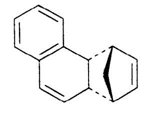
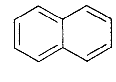
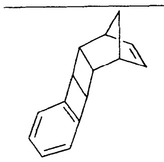
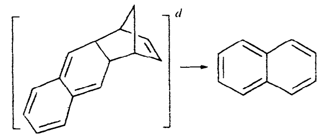
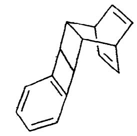
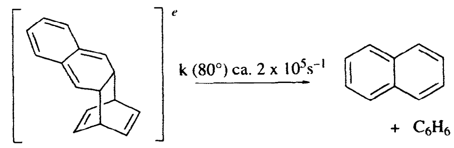
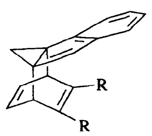
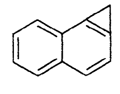
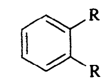
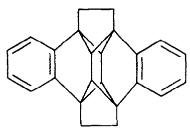
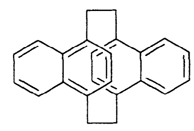
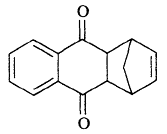
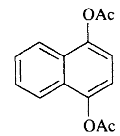
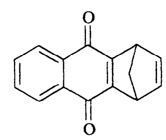
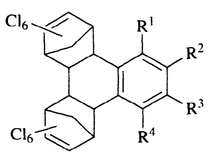
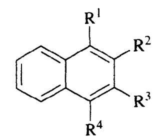
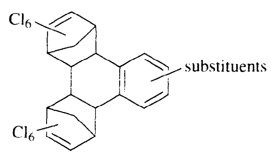
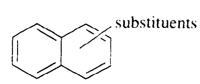
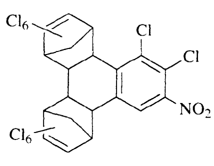
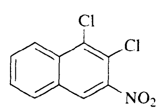
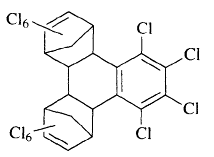
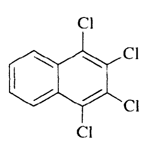
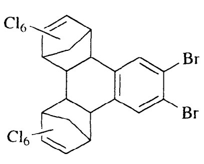
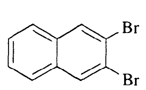
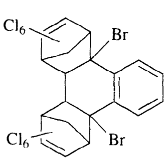
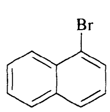
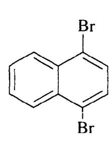
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	E_a = 22.7 $t_{1/2}$ (35°) = 1.7 h	 I (—) + CP (—)	403
	40°	I (—) + CP (—)	907
	heat, >mp	I (—) + CP (—)	908
	Zn, ≥ 35°	I (—) + CP (—)	893
	180°, 1 h	I (30) +  (61)	893
	E_a = 34.8 $t_{1/2}$ (165°) = 20 min	I (—) +  (—)	403
 R^1 R^2: Cl Cl; Ph Ph; Ph *o,o'*-biphenylene	180°, 1 h	 (—) +  (—)	907
	E_a = 22.3 $t_{1/2}$ (40°) = 98 min	I (—) +  (—)	403, 909, 907
	> 112°	 (—) +  (—)	407
	LiCl, DMF	 (—) +  (—)	910
	k (95°) = 1.67 x 10^{-4} s^{-1}	 (—) +  (—)	409, 410
	160°, 90 h k ≤ 10^{-7} s^{-1}	No Reaction	409, 410
	LDA, 68°	 (—) + CP (—)	911
	80 - 92° E_a = 25.77 k (80°) = 10^{-4} s^{-1}	 (100) + CP (—)	275

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	k (80°) = 11 s^{-1}	 [d] (100) + CP (—)	275
	80°	 [e] k (80°) ca. 2 x $10^5 s^{-1}$ (—) + C_6H_6 (—)	275
	FVP, 450°	 R: CN (68), CO_2Me (83) +  (100)	405
	200° / UV (⇌)	 (—)	912
	Ac_2O, heat	 (—) +  (—) + CP (—)	314
	220 - 270°, <1 torr	 **I** + $CPCl_6$ (—)	411
	250 - 400°	 (—) + $CPCl_6$ (—)	412
	400°, vacuum	 (73) + $CPCl_6$ (—)	913
	250 - 400°	 ("only") + $CPCl_6$ (—)	914
	220°	 (63) + $CPCl_6$ (—)	915
	heat, base	 (—) +  (—) + $CPCl_6$ (—)	916

Products **I** (ref. 411):

R^1	R^2	R^3	R^4	**I** (%)
H	NO_2	H	H	90
H	Br	H	H	84
H	Br	Br	H	—
Cl	H	NO_2	H	74
Cl	Cl	Cl	Cl	97

Substituents (ref. 412): none; 2-NH_2; 2,3-$(NO_2)_2$; 1,2-Cl_2-3-NO_2; 1-NO_2; 2-NO_2; 1,3-$(NO_2)_2$; 2-Br; 1,2,3,4-Cl_4; 2,3-Br_2; 2-Br-3-NO_2; 2-SO_2Cl; 2-SO_3H; 2-SO_3H-3-NO_2; 2-NO_2-3-Me; 2-Me; 2-CO_2H; 2-NO_2-3-CO_2H; 2-OH-3-CO_2H; 3-Me-2-OH; 2-I; 2,3-I_2; 2-I-3-NO_2

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS (*Continued*)

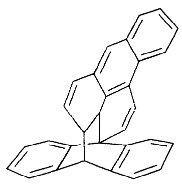
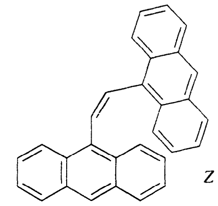
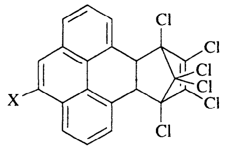
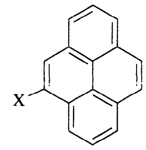
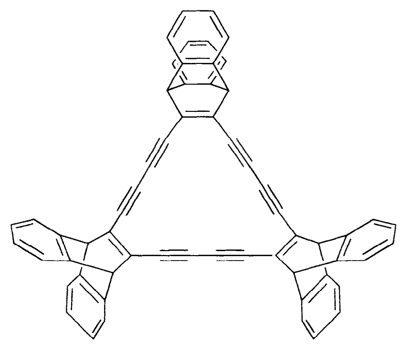
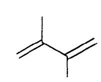
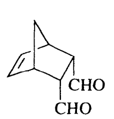
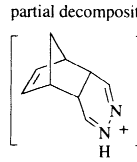
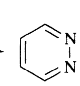
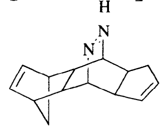
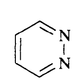
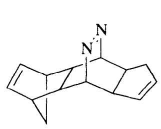
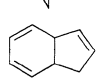
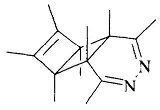
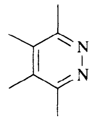
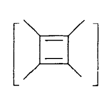
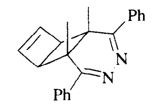
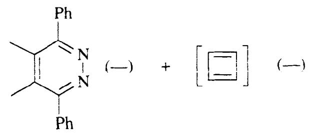
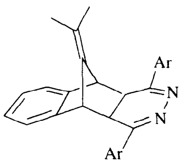
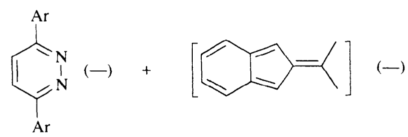
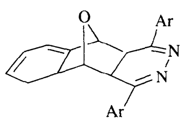
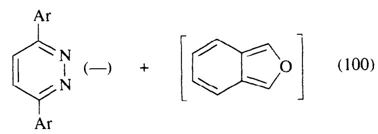
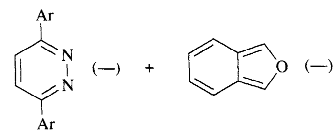
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV (≤ 360 nm) ⇄ UV (≥ 392 nm)	 (50) Z	917
	200°	 X (%): Br 63; Cl 9 + $CPCl_6$ (—)	918, 919
	laser flash pyrolysis	[*cyclo* - C_{18}] (—) + $C_{10}H_{14}$ (—)	413, 414
C_{60}-(2,3-dimethylbutadiene)[f]	rt	C_{60} (—) +  (—)	419
C_{60}-CP cycloadduct	≥ 95° ⇄ rt	C_{60} (—) + CP (—)	419,417, 418
C_{60}-$C_{10}H_{14}$ cycloadduct	≥ 60°	C_{60} (—) + $C_{10}H_{14}$ (—)	419
	112°	C_{60} (—) + $C_{10}H_{14}$ (—)	422
C_{60}-(1,3-diphenylisobenzofuran)	rt	C_{60} (—) + 1,3-diphenylisobenzofuran (—)	419
C_{60}-(C_4H_6) adduct	≥ 100°, TGA[g]	C_{60} (—) + C_4H_6 (—) midpoint 168°	420
C_{60}-CP cycloadduct	≥ 90°, TGA	C_{60} (—) + CP (—) four maxima; midpoint 150°	420
C_{60}-(CP-Me_5)	≥ 160°, TGA	C_{60} (—) + CP-Me_5 (—) two maxima; midpoint 223°	420
C_{60}-$C_{10}H_{14}$	≥ 110°, TGA	C_{60} (—) + $C_{10}H_{14}$ (—) one maximum; midpoint 194°	420
Rb_3C_{60}-(CP-Me_5)	250°, 2 - 5 d	superconductor; attributed to Rb_3C_{60} + CP-Me_5 (—)	420
C_{60}-(CP-Me_5)	200°, 6 h	stable; no reaction	421
C_{60}-CP	200°, 6 h	partial decomposition	421
 + N_2H_4	pH 3 - 4, rt	 →  (—) + CP (—)	197
	pH ≥ 7	 H^+ →  (—) + CP (—)	197
	>400°	 (72) + CP (—)	197
	UV, –196°	 (—) +  (100)	920

TABLE IX. AROMATIC AND HETEROAROMATIC COMPOUNDS *(Continued)*

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat		423
 Ar = 2-pyridyl	50°		424
 Ar = 2-pyridyl	rt, solution		921, 665
	FVP, 120°		921

[a] This intermediate was not detected at 60°.

[b] This compound is stable at –80°.

[c] Both isomers react at the same rate.

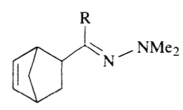
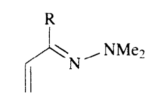
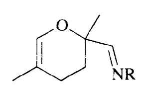
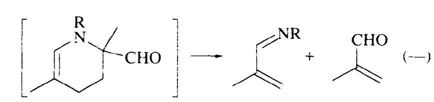
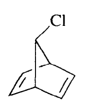
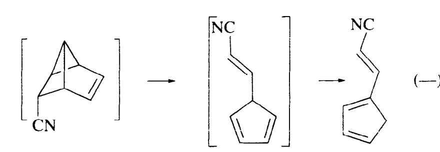
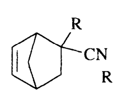
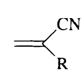
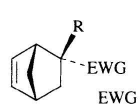
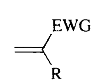
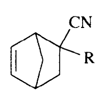
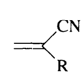
[d] This intermediate can be trapped by fumaronitrile.

[e] This intermediate, which is the "least stable carbocyclic DA adduct", can be trapped by NPM but not by fumaronitrile.

[f] This adduct could not be isolated.

[g] "TGA" is used as an abbreviation for "thermogravimetric analysis".

TABLE X. MONO-EWG SUBSTITUTED ALKENES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	200 - 215°	 R (%): H 53; Me 26 + CP	922
 R = *s*-Bu, Bn, Ph, cyclohexyl, or *t*-Bu	250 - 300°	 (—)	923
	NaCN, aq.EtOH	 (—)	924
 R = Me, Bu, Bn, or allyl	350 - 380°	 (—) + CP	925
 EWG = E or CN; R = Et, *n*-Bu, *n*-C_8H_{17}, or *n*-$C_{12}H_{25}$	625 - 650°, vacuum	 (≥ 50) + CP	926
	190 - 220°	 + CP	927

R	(%)
TMS	75
$TMSOSiMe_2$	81
$TMSO(SiMe_2)_2$	85
$TMSO(SiMe_2)_3$	81
$TMSCH_2$	76
$TMSOSiMe_2CH_2$	57
Et	60
Ph	0
Bn	67

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

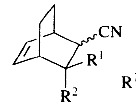
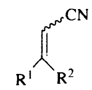
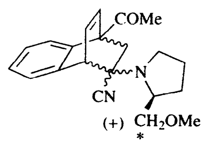
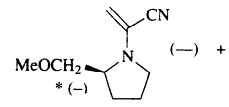
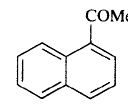
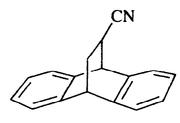
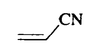
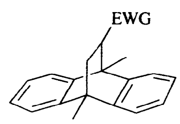
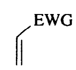
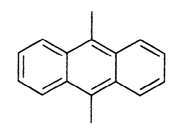
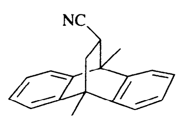
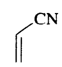
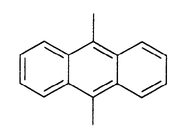
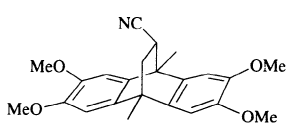
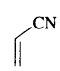
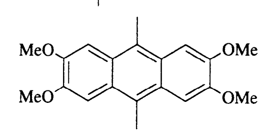
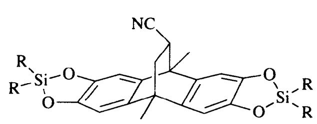
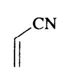
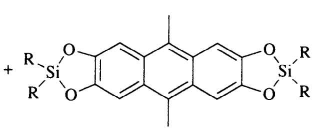
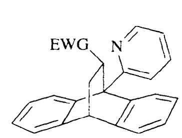
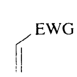
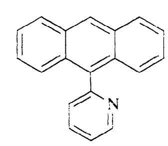
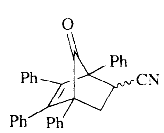
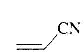
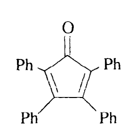
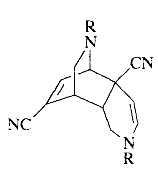
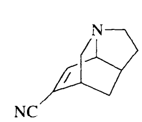
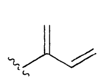
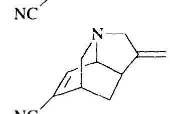
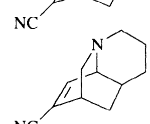
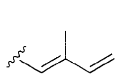
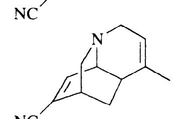
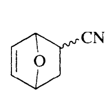
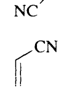
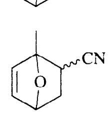
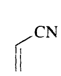
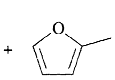
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1, R^2 = H or Me	—[a]	 + C_2H_4 + dienes	313
	40°, C_6D_6 $k = 5 \times 10^{-5}\ s^{-1}$ $t_{1/2}$ = 3.9 h	 + 	928
	250°, Ph_2O k_{rel} = 68 (H = 1)[b] k(250°) = $8.2 \times 10^{-4}\ s^{-1}$	 + $C_{10}H_{14}$	175, 176
	200°, Ph_2O	 +  EWG / k: CN $2.4 \times 10^{-5}\ s^{-1}$ CO_2Et $3.9 \times 10^{-5}\ s^{-1}$	175
	200°, Ph_2O; k_{rel} = 1	 + 	179, 175
	200°, Ph_2O; k_{rel} = 14	 + 	179
	200°, Ph_2O; k_{rel} = 19	 + 	179, 175
	200°, Ph_2O	 +  EWG / 10^5 k (s^{-1}): CN 1.5 CO_2Et 5.2 $CONH_2$ 6.1 CO_2H 17.7	177
	heat[c] ⇌	 + 	439
 R = $(CH_2)_2CH=CH_2$	110°	 (48)	929
R = 	140°	 (10)	929
R = $(CH_2)_3CH=CH_2$	207°	 (8)	929
R = 	207°	 (7)	929
	$\Delta V^{\#}$ = −1.0 to −3.4 $cm^3 \cdot mol^{-1}$ (solvent dependent)	 + furan	930
	$\Delta H^{\#}$ = 25.4 $\Delta S^{\#}$ = −5.5 $\Delta V^{\#}$ = −2 ± 1 cm^3/mol	 + 	931

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

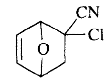
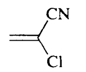
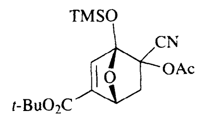
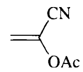
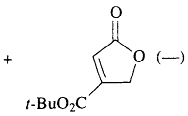
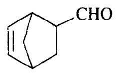
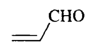
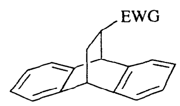
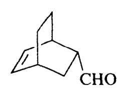
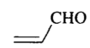
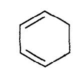
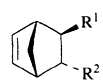
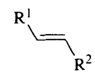
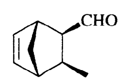
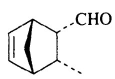
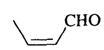
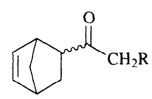
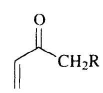
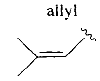
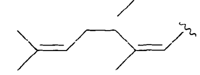
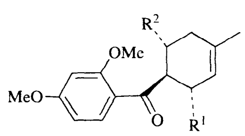
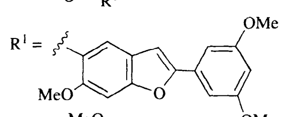
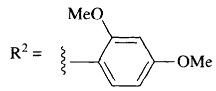
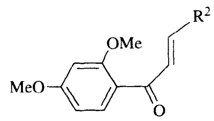
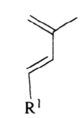
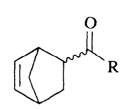
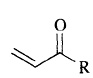
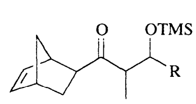
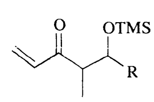
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	K_{eq} (110°) = *ca.* 20 (⇌)	 [d] + furan	932
	rt, aqueous acid	 +  (—)	205
	205 - 242°; E_a = 33.6	 + CP (—)	426, 839
	250°, Ph_2O	 + $C_{10}H_{14}$ EWG / k_{rel} [e]: CHO 251; COMe 179; H 1	175, 176
	292 - 365°; E_a = 46.4	 +  (—)	427
 R^1 / R^2: Me / CHO; CHO / Me	FVP, 500°	 (—) + CP	732
 +  mixture, 1 : 3	FVP, 500°	 (100) + CP	733
	FVP, 450°	 + CP R / (%): Me 96; Et 98; *n*-C_5H_{11} 98; allyl 95;  98;  94	686
 R^1 =  R^2 = 	pyrolysis	 +  (—)	933
	FVP, 500°	 + CP R / (%): *n*-Pr 75; *n*-Bu 91; *n*-C_6H_{13} 94; $(CH_2)_2COMe$ 95; $(CH_2)_2CO_2Et$ 90; $(CH_2)_2COPr$-*n* 93; $(CH_2)_2COBu$-*n* 92; $(CH_2)_2COC_6H_{13}$-*n* 94	934
	500°	 + CP R / (%): Ph 81; Bu 67	935

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

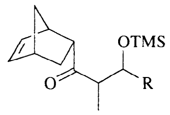
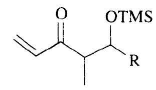
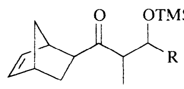
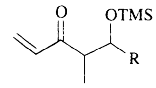
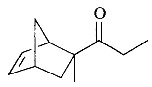
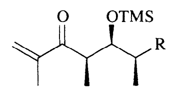
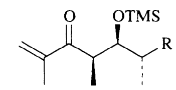
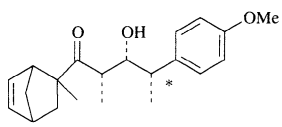
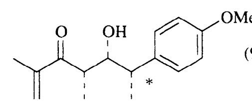
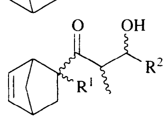
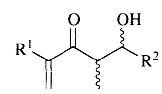
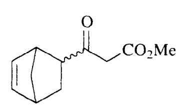
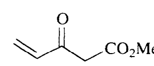
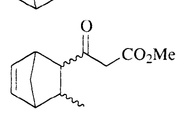
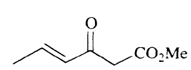
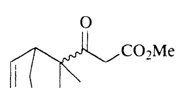
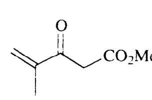
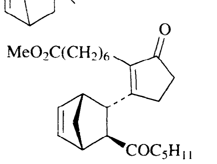
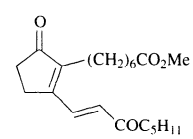
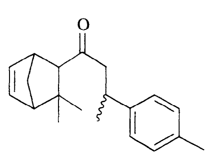
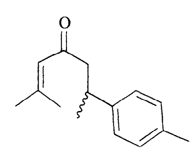
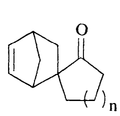
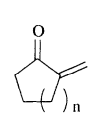
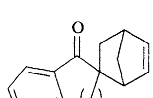
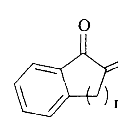
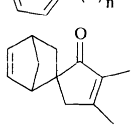
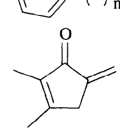
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	500°	 R (%) Ph 80 Bu 71 + CP	935
	500°	 R (%) Ph 80 Bu 75 vinyl 80 + CP	935
	1. $LiN(TMS)_2$ 2. RCH(Me)CHO 3. TMSCl 4. FVP, 500°	 I +  II + CP R — I/II Ph — >98/2 *p*-anisyl — 97/3 $Me_2C{=}CH$ — 95/5 vinyl — 80/20 5-(2-norbornenyl) — 90/10 $PhCH_2OCH_2$ — 12/88 $TBDMSOCH_2$ — 11/89 $(i\text{-}Pr)_3SiOCH_2$ — 15/85	935
	500°	 (90) + CP	428
 R^1 — R^2 H — Ph H — *n*-Bu Me — Ph Me — *n*-Bu Me — 2-furyl	FVP, 450°	 (67 - 95)[f] + CP	937
	FVP, 600°	 (80) + CP	938
	FVP, 600°	 (80) + CP	938
	FVP, 600°	 (80) + CP	938
	180°	 (—) + CP	939
	distill, vacuum	 (46) + CP	940
	FVP, 550°	 n (%) 1 70 3 77 + CP	941
	FVP, 550°	 n (%) 1 95 3 96 + CP	941
	FVP, 550°	 (87) + CP	941

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

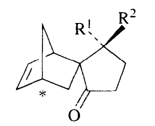
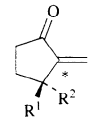
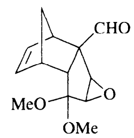
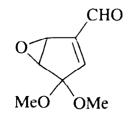
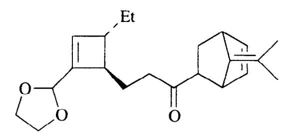
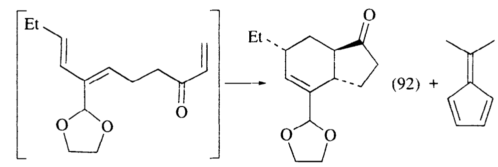
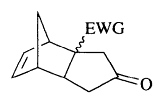
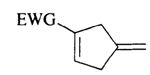
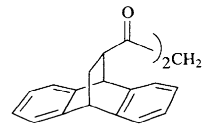
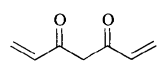
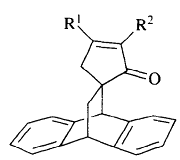
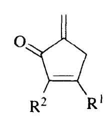
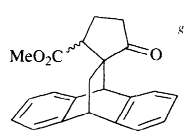
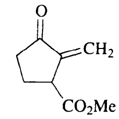
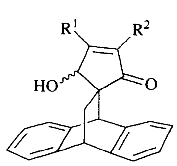
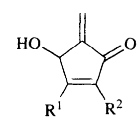
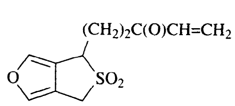
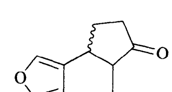
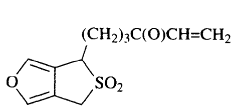
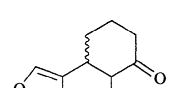
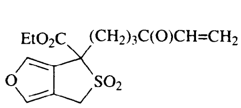
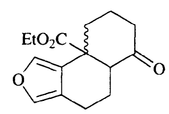
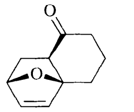
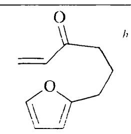
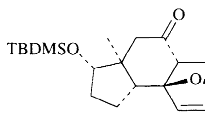
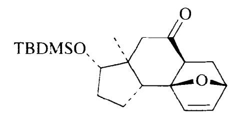
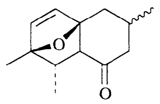
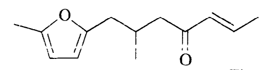
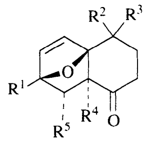
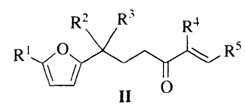
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 650°	 R¹ / R² / (%): H, CO_2Me, 92 (R)-sarcomycin; CO_2Me, H, 93 + CP	698
	FVP, 475°	 (77) + CP	433
	170 - 185°	 (92) +	942, 943
	FVP	 EWG / Temp / (%): CO_2Me, 600°, 89; CO_2Et, 755°, 58; Bz, 560°, 62; SO_2Ph, 560°, 72 + CP	808
	heat	 (56) + $C_{10}H_{14}$	944
 R¹ / R²: Ph, Ph; Me, Ph; H, Ph; H, *m*-anisyl; Me, Me; H, H; Me, H; Et, H	FVP, 400 - 450°	 (ca. 100) + $C_{10}H_{14}$	945
 g	FVP, 450°	 (93) + $C_{10}H_{14}$	946
 R¹ / R²: H, H; Me, H; Me, Me	FVP	 (*ca.* 100) + $C_{10}H_{14}$	187
	1. MVK, rt 2. 180°	 (77) + SO_2 + MVK *cis*/*trans* = 3.2/1	429
	1. MVK, rt 2. 180°	 (59) + SO_2 + MVK *cis*/*trans* = 2.1/1	429
	1. MVK, rt 2. 180°	 (58) + SO_2 + MVK	429

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Florisil, rt, K_{eq} = 7/93	 [h]	192
	80°, 6 d, K_{eq} = 9	 (—)	947
 I	$MeAlCl_2$, CH_2Cl_2, -65° catalyst	 II	182

Time	II/I (0.1 eq. cat.)	II/I (1.1 eq. cat.)
5 min	72/28	61/39
15 min	55/45	81/19
30 min	32/68	78/22
1 h	29/71	67/33
2 h	11/89	72/28
4 h	17/83	70/30

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 I	$MeAlCl_2$, CH_2Cl_2, -65° catalyst	 II	182

R^1	R^2	R^3	R^4	R^5	II/I (0.1 eq. cat.)	II/I (1.1 eq. cat.)
H	H	H	H	Me	31/69	78/22
Me	H	H	Me	H	0/100	19/81
Me	H	H	H	Me	24/76	82/18
H	Me	Me	Me	H	40/60	68/32
H	Me	Me	H	Me	27/73	73/27
Me	Me	Me	Me	H	23/77	78/22
Me	Me	H	H	Me	17/83	78/22

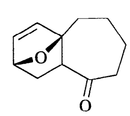
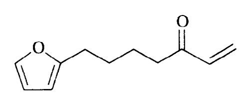
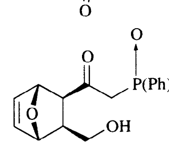
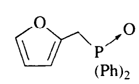
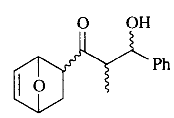
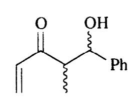
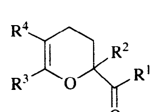
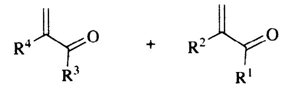
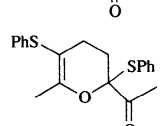
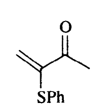
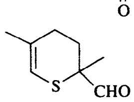
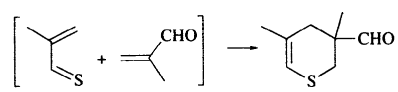
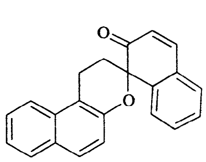
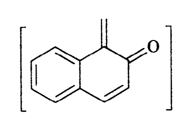
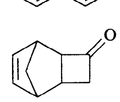
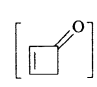
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	– 65°, 0.1 eq. $MeAlCl_2$, K_{eq} = 8/92		182
	130°; exotherm	 (100) + furan	789
	110°	 (70 - 85) + furan	937
 R's = H, Me, and/or Et	UV, 254 nm	 (—)	948
	230° ⇌ 25°, 4 h	 (—)	949
	210°	 (—)	950
	165 - 220°	 (—)	951, 952
	heat	 + CP	953

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

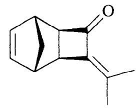
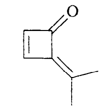
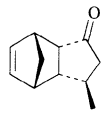
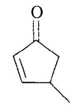
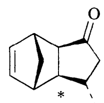
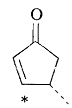
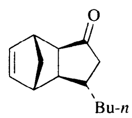
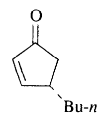
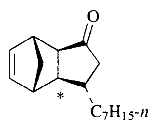
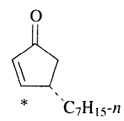
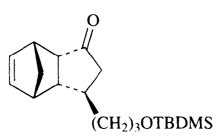
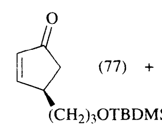
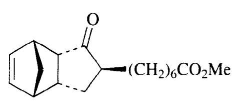
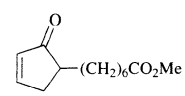
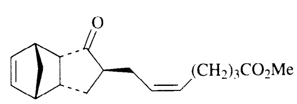
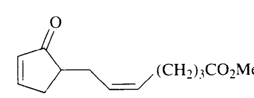
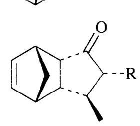
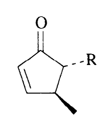
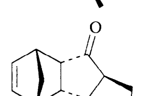
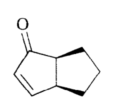
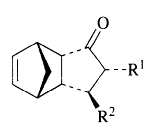
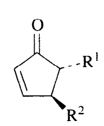
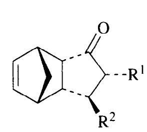
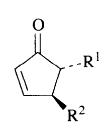
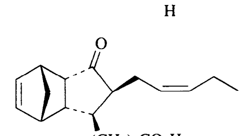
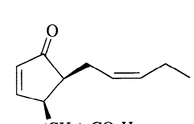
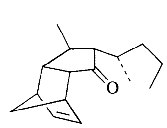
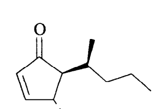
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	flow pyrolysis, 400°	 (—) + CP	954
	BF_3•Et_2O, rt, 6 h	 (70) + CP	217
 + MA (scavenger)	$MeAlCl_2$, 55°	 (70, 93 ee) + (CP-MA)	210
 + MA (scavenger)	$MeAlCl_2$, rt	 (80) + (CP-MA)	208
 + MA (scavenger)	$MeAlCl_2$, 55°	 (71) + (CP-MA)	209
	180°, 5 h	 (77) + CP	212
	300°	 (90) + CP	743
	300°	 (>95) + CP	743
 R = H, Me or (*Z*)-2-pentenyl	FVP, 600°	 (100) + CP	955
	$EtAlCl_2$	 (65) + CP	212
 R^1 / R^2: Et / *n*-Bu $(CH_2)_5CO_2Me$ / *n*-Bu $(CH_2)_7Me$ / *n*-C_8H_{17} $(CH_2)_6CO_2Me$ / *n*-C_8H_{17}	180°	 (≥60) + CP	956
 R^1 / R^2: Et / *n*-Bu *n*-C_5H_{11} / *n*-C_8H_{17} $(CH_2)_5CO_2Me$ / *n*-Bu $(CH_2)_6CO_2Me$ / *n*-C_8H_{17} $(CH_2)_6CO_2Me$ / $CH{=}CHC_6H_{13}$ H / $CH{=}CHC_6H_{13}$	FVP, 500°	 (100) + CP	957
	$EtAlCl_2$, rt fumaronitrile	 (60) + (CP-fumaronitrile)	208
	410°, vacuum	 (94) + CP	958

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

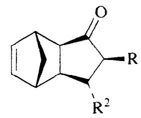
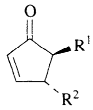
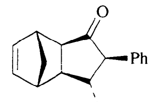
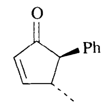
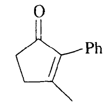
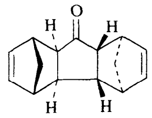
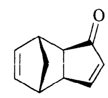
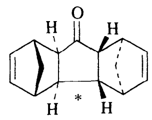
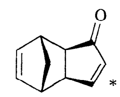
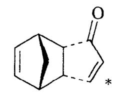
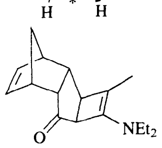
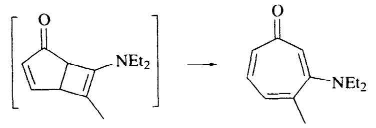
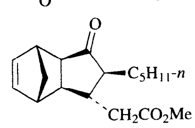
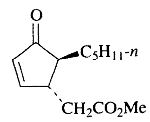
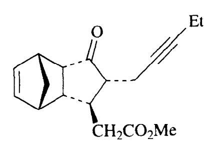
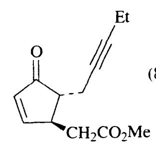
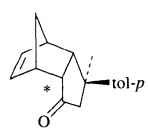
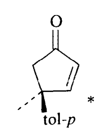
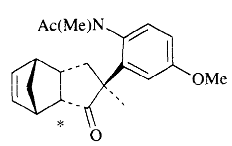
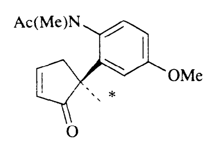
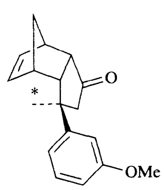
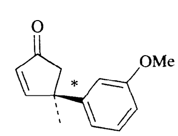
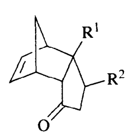
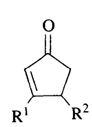
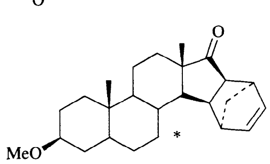
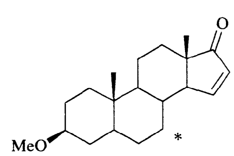
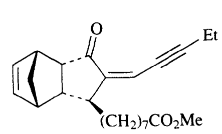
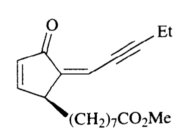
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 600°	 R[1] / R[2] / (%): *n*-Bu, H, 79; *n*-Bu, Me, 79; *n*-Bu, *t*-Bu, 93 + CP	959
	FVP, 600°	 (23) +  (70) + CP	959
	$BF_3 \cdot Et_2O$, rt, 4 h	 (—) + CP	217
	180°	 (62) +  (9) + CP	441
	FVP, 600°	 (20) + CP	960
	heat, vacuum	 (—) + CP	961
	FVP, 430°	 (81) + CP	962
	179°	 (—) + CP	963
	179°, 11 h	 (66) + CP	964
	180°	 (87) + CP	965
 R^1 = H, CO_2Me, or CO_2Et; R^2 = Me, C_7H_{15}, or $CH(CO_2Me)_2$	FVP, 500°	 (80 - 100) + CP	433
	heat	 (—) + CP	966, 967
	254°, vacuum	 (73) + CP	968

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

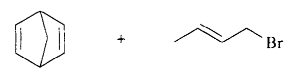
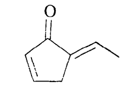
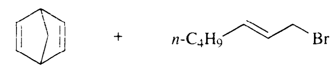
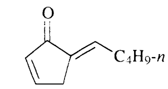
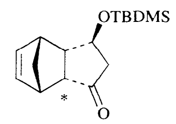
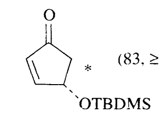
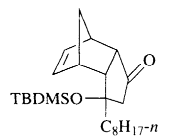
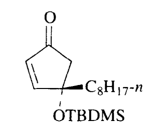
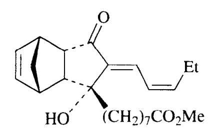
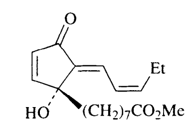
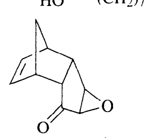
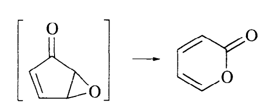
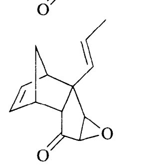
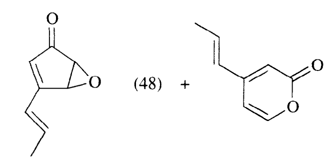
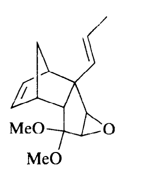
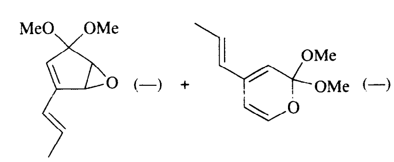
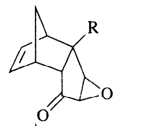
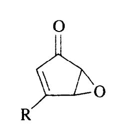
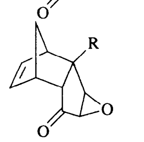
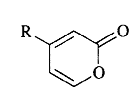
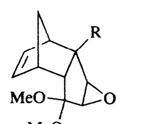
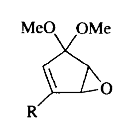
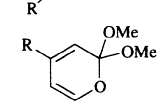
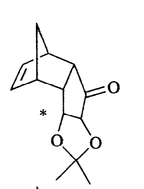
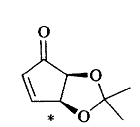
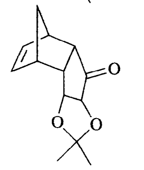
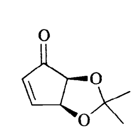
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Pd(Ph)_4$, CO	 (34) + CP	221
	$Pd(Ph)_4$, CO	 (20) + CP	221
	420°, 1 min	 (83, ≥ 98 % ee) + CP	969
	400°	 (83) + CP	970
	240°, 5 min	 (64) + CP	971
	380 - 440°	 (—) + CP	431
	FVP, 420°	 (48) + (10) + CP	430
	FVP, 450°	 (—) + (—) + CP	430
	FVP, ≤ 430°	 R (%): CO_2Et 55; CHO 95 + CP	432
	FVP, ≥ 510°	 R (%): CO_2Et 95; CHO 95; CH_2OH 80 + CP	432
	FVP, ≤ 430°	 R (%): CO_2Et 65; CHO 90 + CP	432, 433
	FVP, ≥ 510°	 R (%): CO_2Et 60; CHO 55; CH_2OH 65 + CP	432
	180°	 (65) + CP	972
	180°	 (40) + CP	973

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

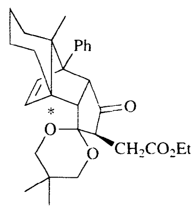
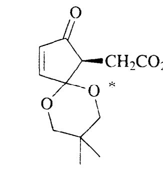
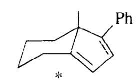
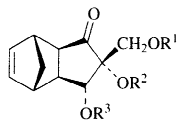
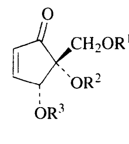
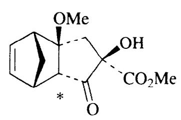
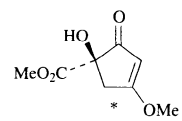
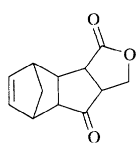
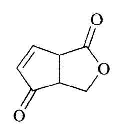
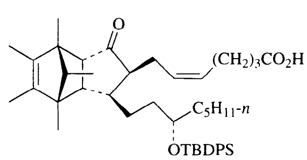
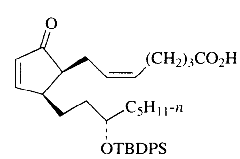
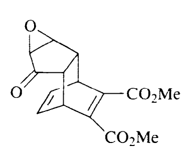
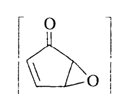
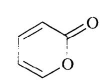
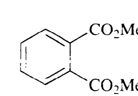
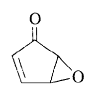
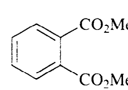
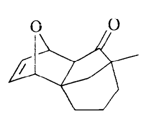
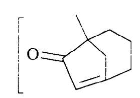
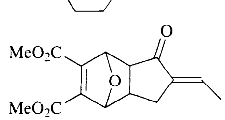
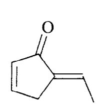
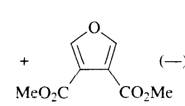
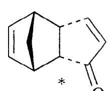
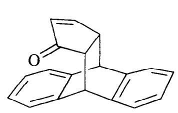
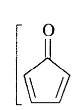
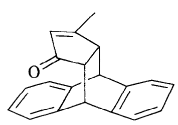
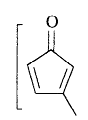
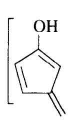
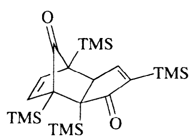
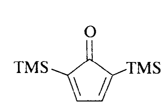
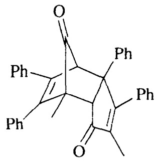
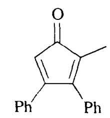
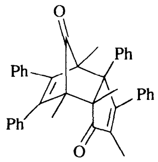
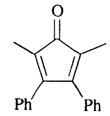
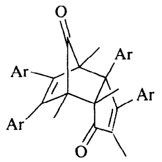
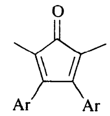
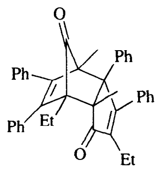
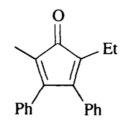
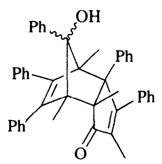
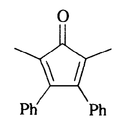
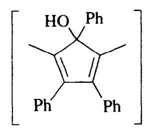
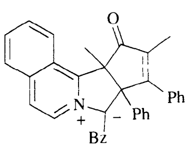
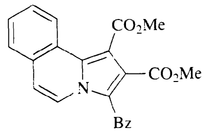
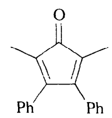
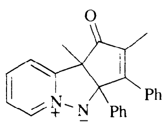
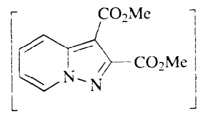
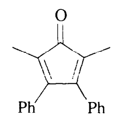
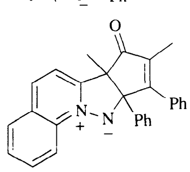
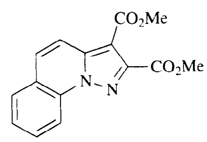
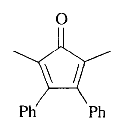
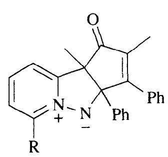
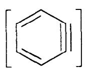
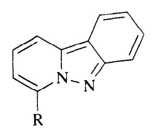
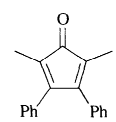
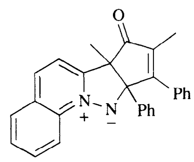
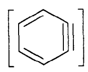
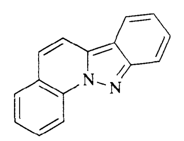
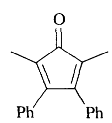
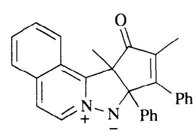
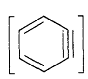
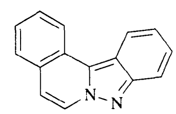
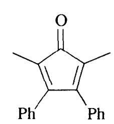
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	300°	 ("high") +  (—)	974
 R¹ R² R³: H H H; Ac Ac Ac; Me H H; Me H Ac; Me Ac Ac	FVP, 525°	 (*ca.* 100) + CP	975
	FVP, 500°	 (100) + CP	145
	220°, vacuum	 (96) + CP	976
	3.5 eq. Me_2AlCl, −10°, 48 h 5 eq. fumaronitrile	 (70) + (CP-Me_5)-fumaronitrile	211
	410°	 →  (—) + 	431
	180°	 (98) + 	431
	240°	 (—) + furan	977
	0.3 N HCl, *n*-BuOH, 50°	 (—) +  (—)	203
	—	Used in multistep synthesis of (−)-goniomitine.[i]	978
	350°	 (—) + $C_{10}H_{14}$	979
	230°	 →  + $C_{10}H_{14}$	980, 89
	FVP, 550° ⇌	 (—)	435

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	dissolve ⇌	 (—)	981
	heat in solution ⇌ cool	 (—)	982, 983, 381
 Ar = Ph or *p*-tolyl	150°	 (—)	984
 Ar = Ph or *p*-tolyl	150°	 (—)	984
	rt	 (—) + 	983
 + DMAD	—	 (—) +  (—)	985
 + DMAD	112°	 +  (—)	986
 + DMAD	112°	 (64) +  (—)	986
 + 	heat	 R (%) H 14 Me 20 +  (—)	987
 + 	heat	 (57) +  (—)	987
 + 	heat	 (59) +  (—)	987

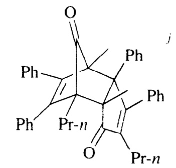
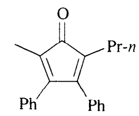
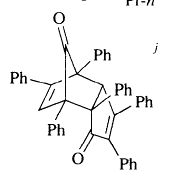
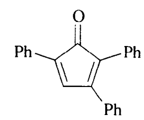
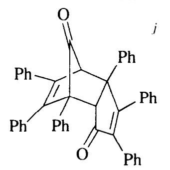
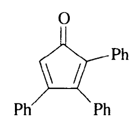
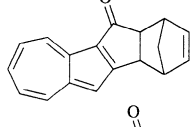
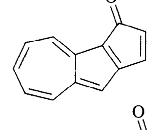
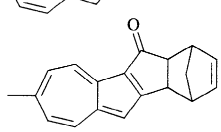
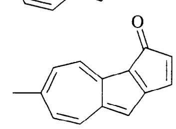
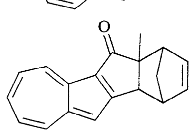
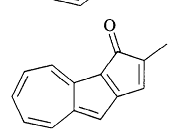
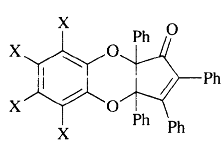
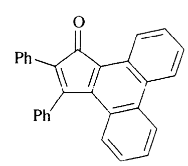
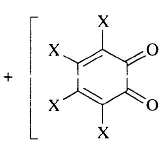
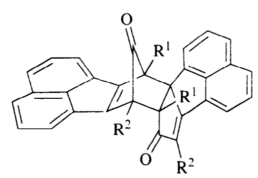
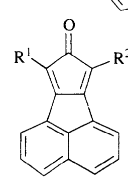
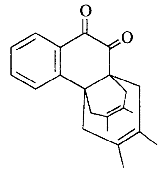
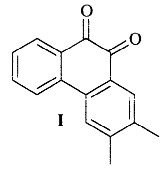
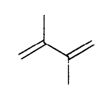
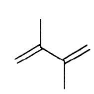
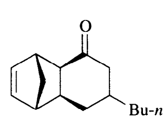
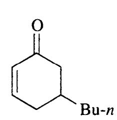
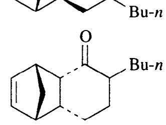
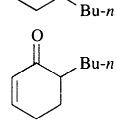
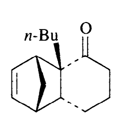
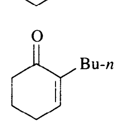
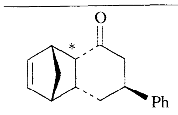
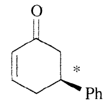
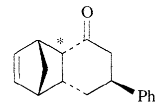
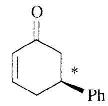
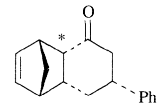
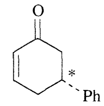
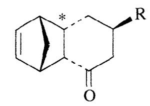
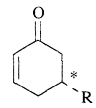
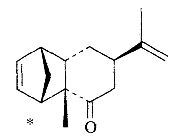
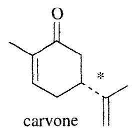
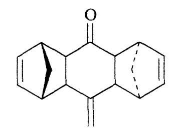
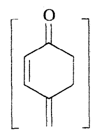
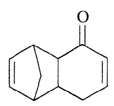
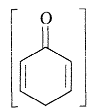
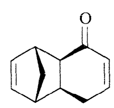
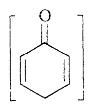
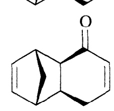
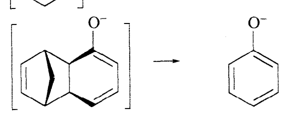
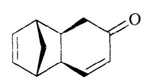
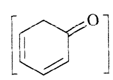
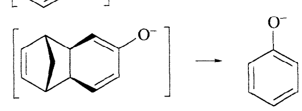
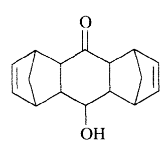
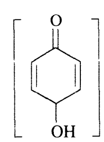
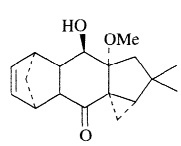
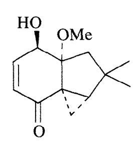
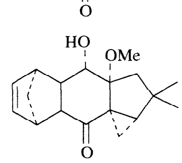
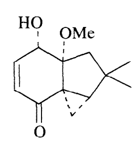
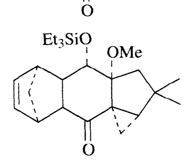
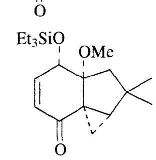
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 [j]	dissolve ⇌	 (—)	988
 [j]	dissolve ⇌	 (—)	989
 [j]	warm in solvent	 (—)	990
	FVP, 550°	 (83) + CP	991
	FVP, 550°	 (95) + CP	991
	FVP, 550°	 (84) + CP	991
	heat	 (—) + 	992
 R[1] / R[2]: Me / Me; Et / Et; n-Pr / n-Pr; n-C_6H_{13} / n-C_6H_{13}; Me / Ph	dissolve ⇌		993
	≥ 135° (oxid.)	 I (72) + 	994
	heat, CrO_3, HOAc	I (91) + 	994
	$MeAlCl_2$, 60°, 1.5 h; 5 eq. MA	 (86) + CP-MA (—)	208
	$MeAlCl_2$, 55°, 1.5 h; 5 eq. MA	 (89) + CP-MA (—)	208
	$MeAlCl_2$, 55°, 1.5 h	 (—) + CP	208

TABLE X. MONO-EWG SUBSTITUTED ALKENES *(Continued)*

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	$BF_3 \cdot Et_2O$, rt	 (72) + CP	218
	heat	 (—) + CP	995
	heat	 (—) + CP	995
	250°	 (—) + CP	744
	230°	 carvone (88, >99% ee) + CP	744, 996
	FVP, 680°	 (—) + CP	857
	FVP, 800°	 (—) + CP	605
	FVP, 200°	 (—) + CP	229
	OH^-; gas phase	 (—) + CP	229
	FVP, 200°	 (—) + CP	229
	OH^-; gas phase	 (—) + CP	229
	FVP, 800°	 (—) + CP	605, 857
	FVP, 570°	 (96) + CP	997, 998
	FVP, 560°	 (96) + CP	997, 998
	FVP, 560°	 (100) + CP	997, 998

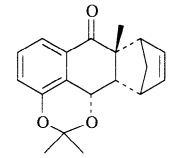
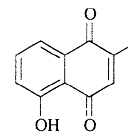
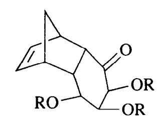
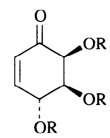
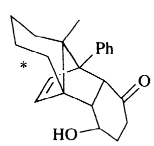
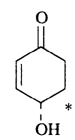
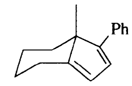
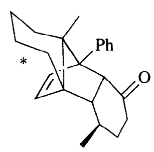
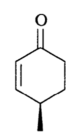
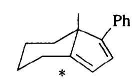
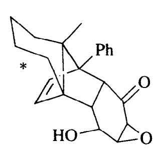
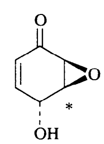
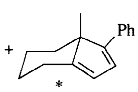
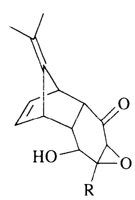
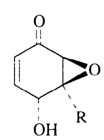
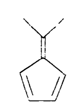
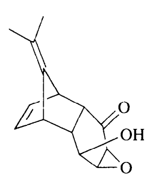
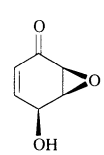
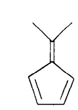
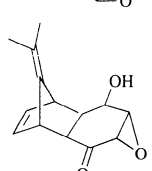
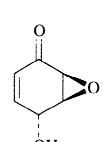
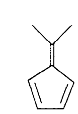
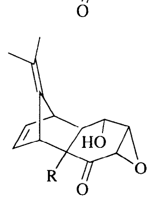
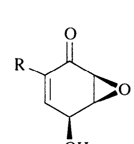
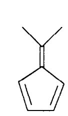
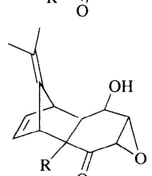
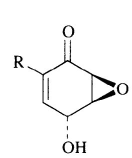
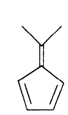
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 270° 2. oxidation	 (49) + CP	999, 943
 R = CH_2OMe	250°	 (95) + CP	1000, 744
	250°, vacuum	 (54, >98 ee) + 	457
	300°	 ("high") + 	974
	FVP, 300°	 (90) + 	442
	heat	 R / Temp / (%) H / 160° / 100 Me / 190° / 43 + 	1001
	160°	 (100) + 	1001
	180°	 (100) + 	1001
	heat	 R / Temp / (%) Me / 170° / 100 CH_2OH / 140° / 65 + 	1002, 460, 1003
	heat	 R / Temp / (%) Me / 170° / 100 CH_2OH / 140° / 70 + 	1002, 460, 1003

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

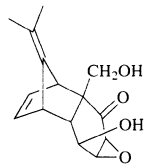
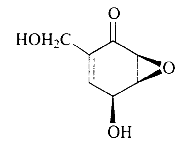
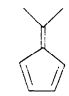
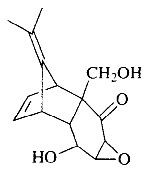
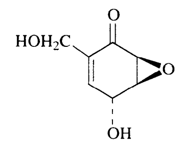
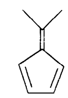
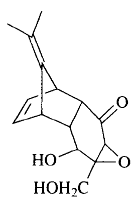
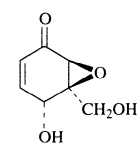
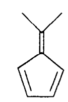
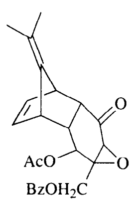
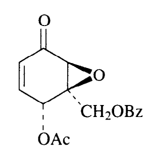
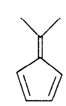
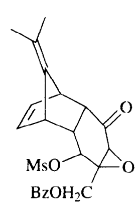
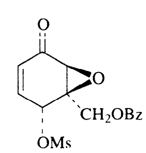
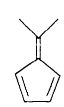
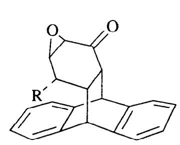
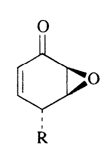
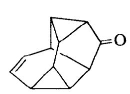
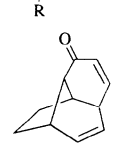
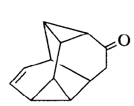
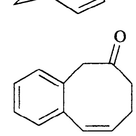
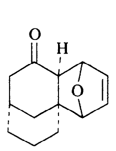
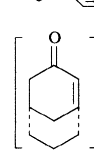
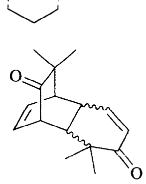
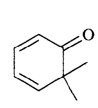
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140°	 (60) + 	1002, 460, 943
	115°	 (76) + 	1002, 460
	140°	 (—) + 	1004
	160°	 (78) + 	1005, 1006
	120°	 (78) + 	1007, 1008
	heat, vacuum	 R / Temp / Press / (%): OH, 460°, 0.2 Torr, 98; O_2CNHMe, 400°, 0.4 Torr, 80 + $C_{10}H_{14}$	1009
	FVP, 400°	 (84)	1010
	FVP, 400°	 (80)	1010
	330 - 380°	 (—) + furan	1011
	400°	 (—)	237

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

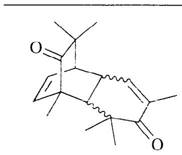
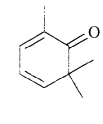
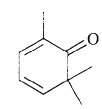
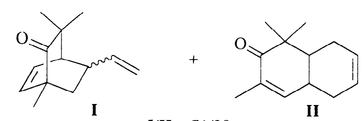
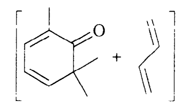
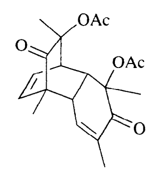
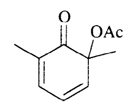
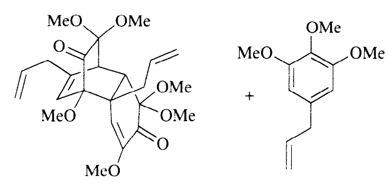
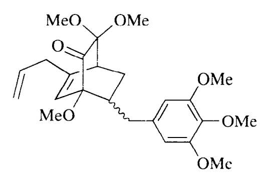
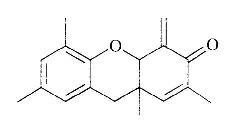
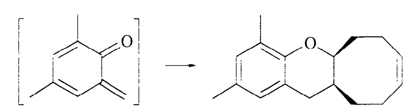
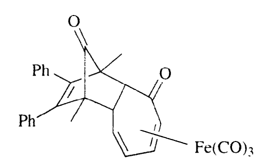
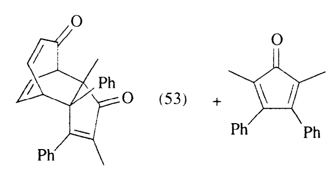
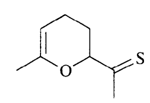
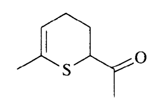
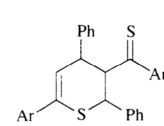
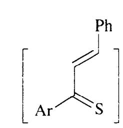
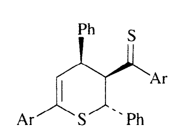
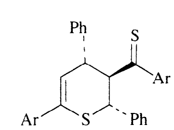
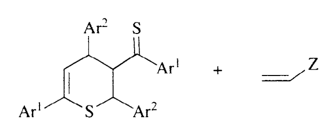
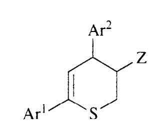
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	280°	 (—)	1012
	150° ⇄ rt (slow)	 (—)	1013
 I + II, I/II = 71/29	150°	 ⟶ I/II = 62/38	1013
	180°, vacuum		1014, 1015, 1016
	180°	 (%): *exo* 13, *endo* 14	1017
 + COD	heat	 (—)	1018
	Ce(IV), 0°	 (53) + (dimer, 29)	155
	reflux, 1 h[k]	 (25)	1019
 Ar = Ph, *p*-anisyl, *p*-ClC_6H_4	80°	 Ar (%): Ph 44; *p*-anisyl —; *p*-ClC_6H_4 —	1020, 1021, 1022
 Ar = *p*-anisyl	heat	 (—)	1023
 Ar^1, Ar^2 = various aryl; Z = CN, CHO, Ac, CO_2Me	reflux	 ("excellent")	1024

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

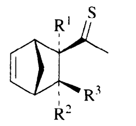
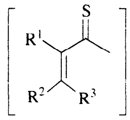
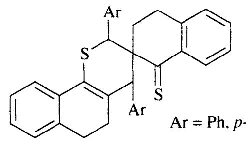
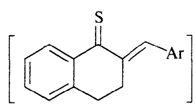
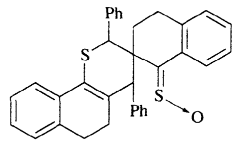
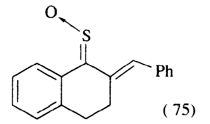
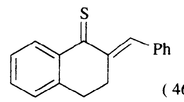
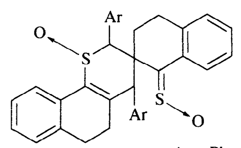
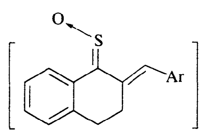
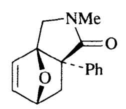
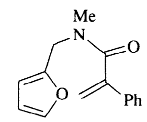
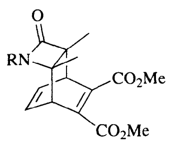
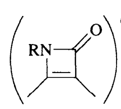
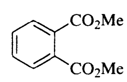
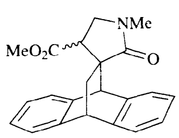
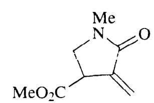
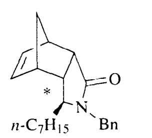
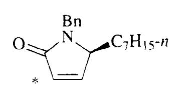
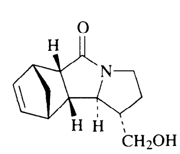
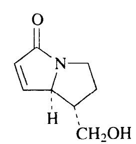
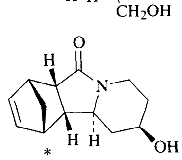
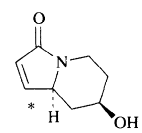
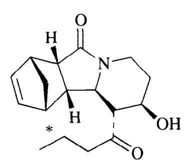
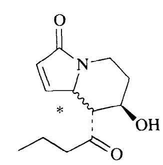
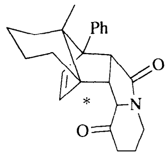
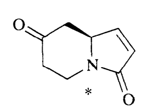
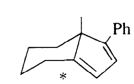
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1 / R^2 / R^3: H / H / H; H / Me / H; Me / H / H; H / Me / Me	FVP, 500°	 (—) + CP	1025, 1026
 Ar = Ph, *p*-anisyl, *p*-ClC_6H_4	80°	 (—)	1021, 1020, 1022, 1027
	138°	 (75) +  (46)	1028
 Ar = Ph or *p*-ClC_6H_5	138° ⇌	 Ar (%): Ph ≥78; *p*-anisyl —	1028, 1029, 1030
	C_6D_6, 120°, K_{eq} = 1.08 ⇌		876
 R = H or Me	200 - 325°	 +  (—)	1031
	FVP, 450°	 (—) + $C_?H_{10}$	1032
	FVP, 450°	 (76, ≥74 % ee) + CP	1033, 1034
	FVP, 500°	 (86) + CP	1035
	FVP, 450°	 (83) + CP	1036, 1035
	FVP, 435°	 (99, 3/1 mixture diast.) + CP	1036, 1037
	heat	 (—) + 	1038

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

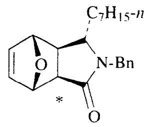
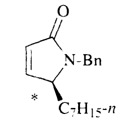
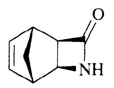
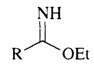
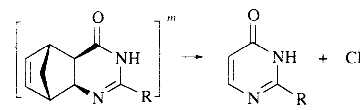
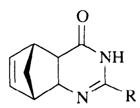
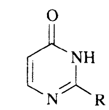
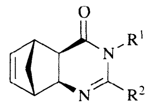
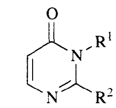
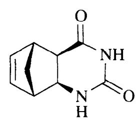
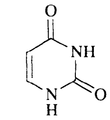
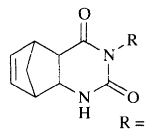
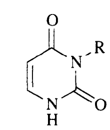
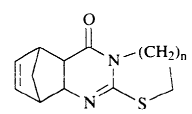
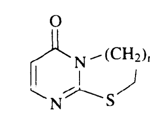
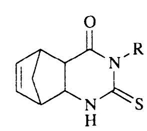
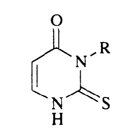
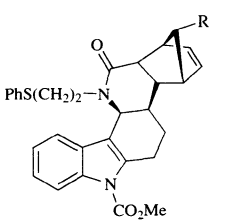
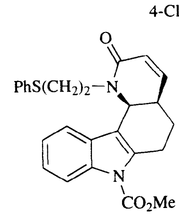
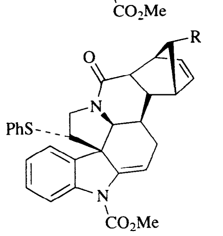
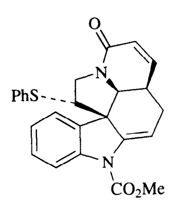
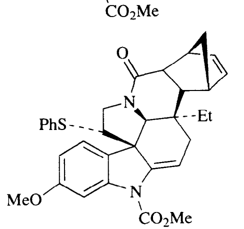
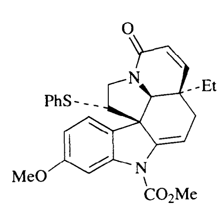
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	160°, 0.5 h	 (71) ≥97% ee + furan	1033, 1034
 + 	132°	 + CP R (%) Me 82 Et 78 C_6H_{11} 92 *p*-ClBn 80 Ph 88 *p*-ClC_6H_4 85 *m*-ClC_6H_4 83 *p*-tolyl 90	1039
 *endo,endo* or *exo,exo*	132°	 R as above (78 - 90) + CP	1040, 1041, 1042
 R^1 = Me, Ph, or Ar R^2 = H, Me, or Et	*ca.* 140°	 (42 - 62) + CP	1043, 1044
	140°	 (—) + CP	1045
 R = Ph, *p*-Cl-C_6H_4, *p*-tolyl, Bn, or Me	210 - 240°	 (65 - 85) + CP	1046, 1047
	140°, 20 min	 + CP n (%) *exo* 80 *exo* 2 83 *endo* 1 70 *endo* 2 75	1048
 di-*endo* or di-*exo*	heat, ≥ mp	 + CP R (%) Me 54 Et 83 Ph 80 *p*-tolyl 85 4-ClC_6H_4 85	1049, 1050
	heat	 + CP or CPTMS R Temp Time (%) H 180 - 190° 120 h 67 TMS 180 - 190° 7 h 100	258, 1051
	heat	 + CP or CPTMS R Temp Time (%) H 190 - 200° 24 h ≥95 TMS 110° 1.5 h 100	258, 1051
	200°	 (86) + CP	1052

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

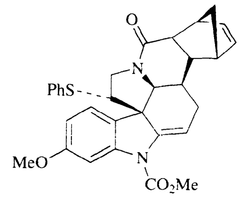
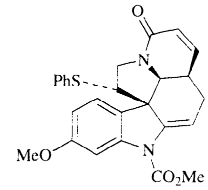
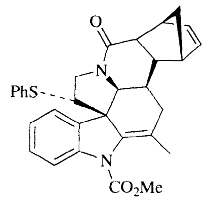
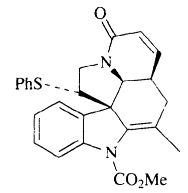
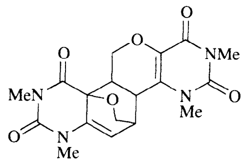
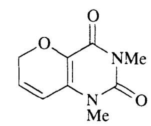
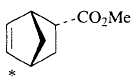
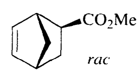
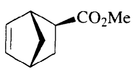
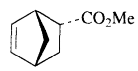
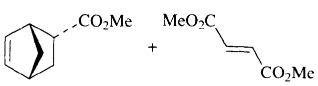
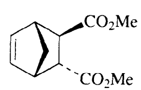
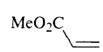
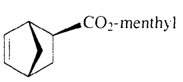
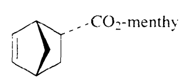
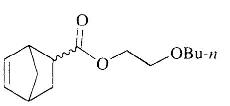
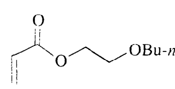
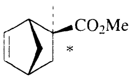
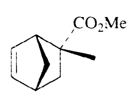
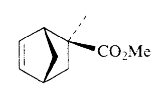
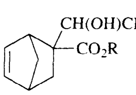
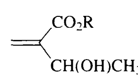
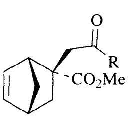
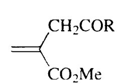
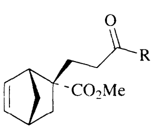
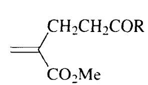
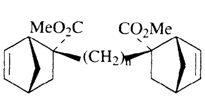
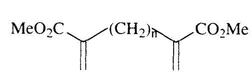
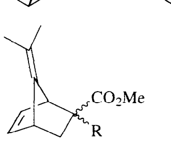
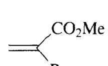
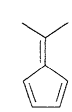
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	190°	 (88) + CP	1052
	200°	 (69) + CP	1053
	130° ⇌	 (—)	1054
	171°	 (—)	1055
	alumina	 (—)	191
	alumina	 (—) + 	189
	alumina ⇌		190
	450°, 8 Torr	 (92) + CP (85)	1056
	171°	 *rac* (7) +  *rac* (5.6)	1057, 1055
 R = *n*-Bu, *i*-Bu, *i*-Amyl, $CH_2CH(Me)Et$, or CH_2CHEt_2	heat	 (—) + CP	1058
	625 - 650°, vacuum	 R (%): Me 60; OEt 70 + CP	1059
	625 - 650°, vacuum	 R (%): Me 85; OEt 75 + CP	1059
	680°	 (—)	926
	170 - 190°	 R (%): Me 70; Et 58; allyl 31; 2-butenyl 35; Bn 83; EtO_2CCH_2 55 +  (—)	1060, 943

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

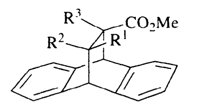
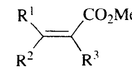
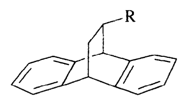
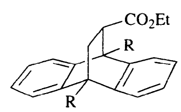
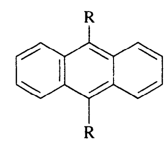
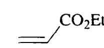
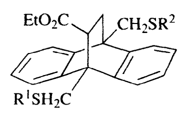
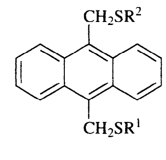
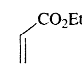
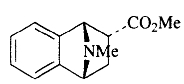
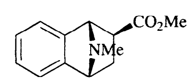
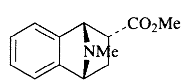
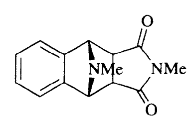
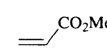
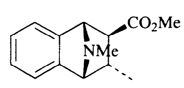
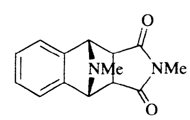
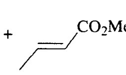
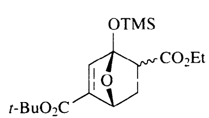
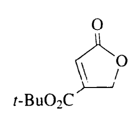
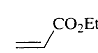
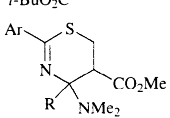
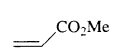
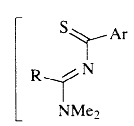
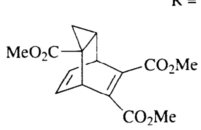
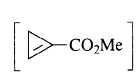
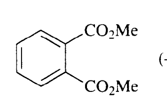
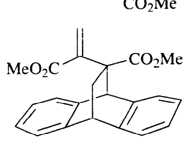
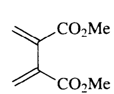
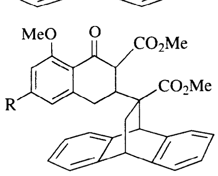
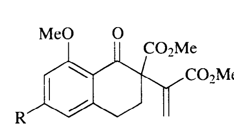
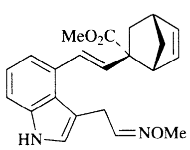
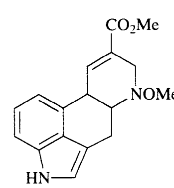
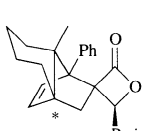
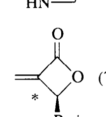
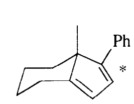
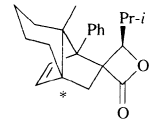
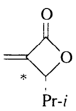
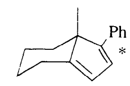
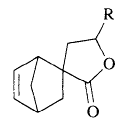
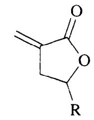
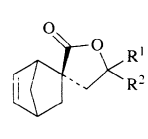
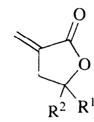
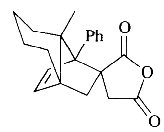
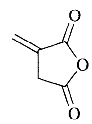
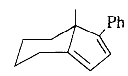
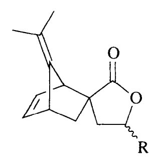
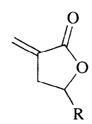
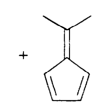
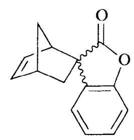
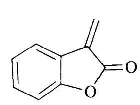
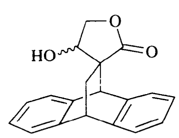
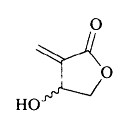
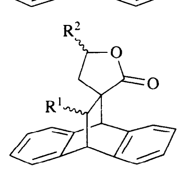
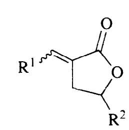
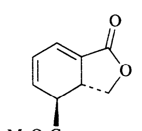
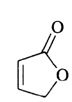
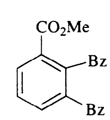
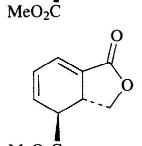
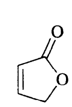
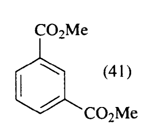
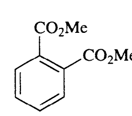
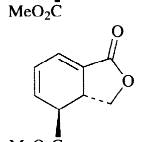
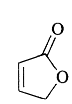
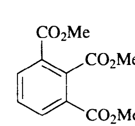
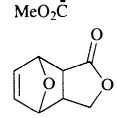
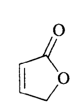
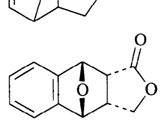
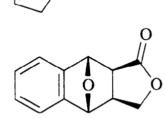
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1 R^2 R^3: H H H; H D D; D H H	300°	 + $C_{10}H_{14}$ (—)	1061
 R = CO_2Me, $CONH_2$, CO_2H	250° [a]	 + $C_{10}H_{14}$	175, 176
 R = 21 substituents	200° [a]	 (—) + 	175, 176
	200°	 (—) R^1 / R^2 / $10^5k(s^{-1})$: Me / Me / 26.4; *t*-Bu / *t*-Bu / 48.4; —$(CH_2)_8$— / 40.3; —$(CH_2)_{10}$— / 40.3 + 	175
	rt, $LiClO_4$ / ether, K_{eq} = 19	 (—)	220
 + NMM	rt, $LiClO_4$ / ether, K_{eq} = *ca.* 3	 (—) + 	220
 + NMM	rt, $LiClO_4$ / ether	 (—) + 	220
	H_3O^+, rt	 (—) + 	205
 R = H, Me, or CO_2Et	140°	 + 	1062
	200 - 300°	 +  (—)	764, 765
	FVP, 400°	 (100) + $C_{10}H_{14}$	1063
	FVP	 R (%): H 85; Me 89 + $C_{10}H_{14}$	1063
	200°	 (67) + CP	1064
	FVP, 300°	 (71, 99% ee) +  (92)	1065

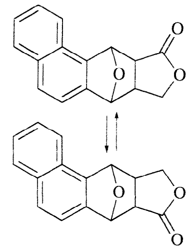
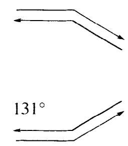
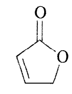
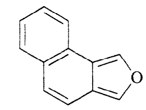
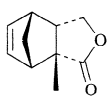
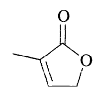
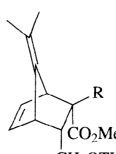
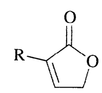
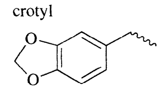
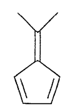
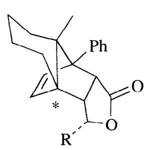
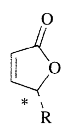
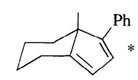
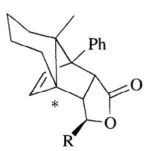
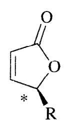
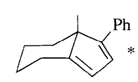
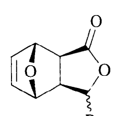
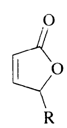
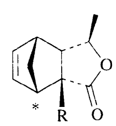
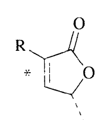
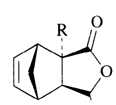
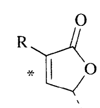
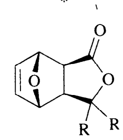
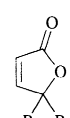
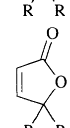
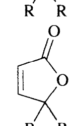
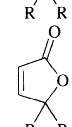
TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 300°	 (74, 99% ee) +  (92)	1065
	625 - 650°, vacuum	 R (%): H 85; Me 75 + CP	1059
	heat	 R^1 R^2 (%): H H 100; Me Me 100; Ph Ph 100; Me H 100; *i*-Bu H 100 + CP	710
	rt, 1 atm (slow) ⇌ rt, 6.5 kbar, 10 d (88%)	 (—) +  (—)	1066
	140°, 0.5 h	 R (%): H 70; Me 60; Et 54; Ph 80 + 	1067
	FVP, 700°	 (—) + CP	1068
	FVP	 (—) + $C_{10}H_{14}$ *rac* tuliapin	1069
	250 - 300°	 R^1 R^2 (%): H H 77; *cis*-CO_2Me H 74 *Z*; *trans*-CO_2Me H 65 *E*; H Me 81; *cis*-CO_2Me Me 78 *Z*; *trans*-CO_2Me Me 81 *E* + $C_{10}H_{14}$	1070
 + Bz—≡—Bz	140°, 40 h	 +  (60)	693
 + ≡—CO_2Me	140°, 40 h	 +  (41) +  (10)	693
 + DMAD	140°, 40 h	 +  (61)	693
	140°, 20 Torr	 (65) + furan (80)	1071
	190°	 (—)	1072

254

255

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	131°  131°	 (—) +  (—)	1073
	FVP, 500°	 (80) + CP	1074
 R, CO_2Me, CH_2OTHP	heat, sealed tube	 R | Temp | (%): Me | 280° | 50; crotyl | 280° | 60;  | 210° | 87 + 	1075, 943
 R = Me or *n*-Bu	250°	 (—) + 	759, 1038
 R = Me, Et, *i*-Pr, *i*-Bu, or *n*-Bu	250°	 (85-90, 100% ee) + 	759, 1038, 974
 R = alkyl or allylic	135 - 150°	 I (70-100) + furan	1076
R = *i*-Pr or *s*-Bu	130°	I (100) + furan	1077
	heat	 R | Temp | (%): Me | 285° | 88; Et | 285° | 87; Bu | 240° | 80; Bu | 285° | 99 + CP	1078
	heat	 R | Temp | (%): Me | 285° | 89; Et | 285° | 86; Bu | 240° | 60; Bu | 285° | 83 + CP	1078
 R = *n*-Pr, *n*-Bu, *n*-C_5H_{11}, *n*-C_6H_{13}, Ph, or Bn R,R = —$(CH_2)_4$— or —$(CH_2)_5$—	130°	 (100) + furan	1077
R = R = alkyl or allyl (7 examples)	135 -150°	 (95 - 100) + furan	1079
R = R = Ph, *p*-ClC_6H_4, *o*- or *p*-tolyl	130°	 (90 - 96) + furan	1080
	130°	 R,R | (%): —$(CH_2)_5$— | 98; —$(CH_2)_6$— | 97 + furan	1081

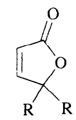
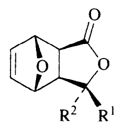
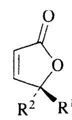
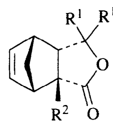
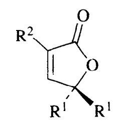
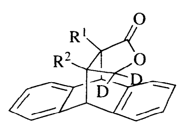
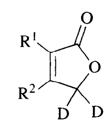
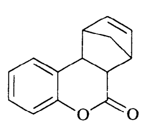
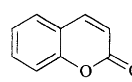
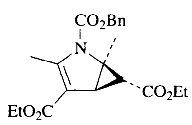
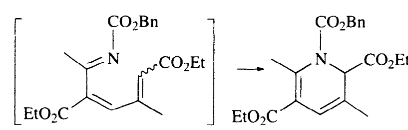
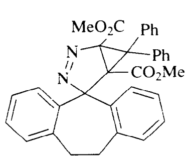
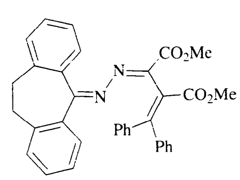
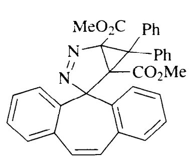
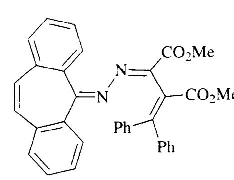
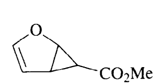
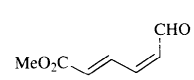
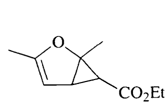
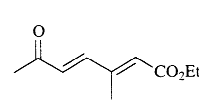
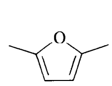
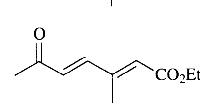
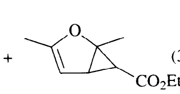
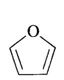
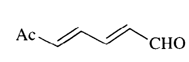
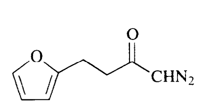
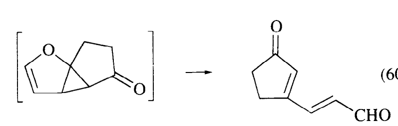
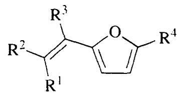
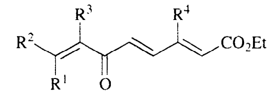
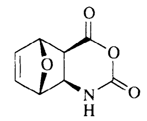
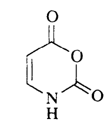
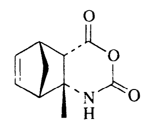
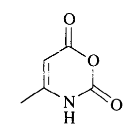
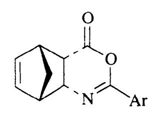
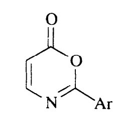
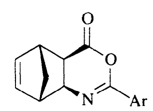
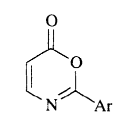
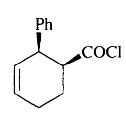
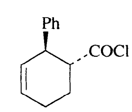
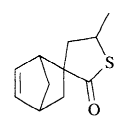
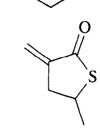
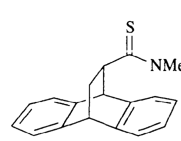
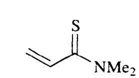
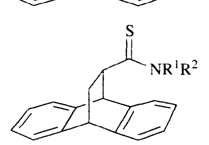
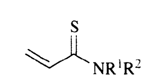
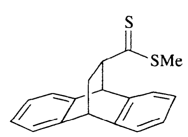
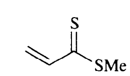
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
R = Et, Pr, *n*-Bu, *n*-C_5H_{11}, *n*-C_6H_{13}, *i*-Bu, allyl, Bn, *p*-tolyl, Ph, *o*-tolyl, or *p*-chlorophenyl	150°	 (—) + furan	1082
 R¹ R²: *n*-Bu Me; Et Me; Me *n*-Bu; Me Et; Me *i*-Pr *; Et *n*-Bu; *n*-Bu Et	110°	 (85 - 95) + furan	1083
 R^1 = H, alkyl, or aryl R^2 = alkyl, allyl, Bn, Ar 10 examples	280°	 (—) + CP	1084
	300 - 350°	 R¹ R² (%): H H 80; Me H 65; H Me 65 + $C_{10}H_{14}$	339
	150°	 (90) + CP	1085
	260°	 (99)	1086
	UV	 (15)	1087
	UV	 (53)	1087
	140 -160°	 (100)	1088
	silica gel	 (87)	1089
 + N_2CHCO_2Et	Cu bronze	 (38) +  (36)	1089
 + N_2CHAc	Cu bronze, 90°	 (43)	1090
	Cu(II)	 (60)	1091

TABLE X. MONO-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + N_2CHCO_2Et	50 - 70°	 R[1] R[2] R[3] R[4] (%) Me Me H H 47 Me H H H 46 Me H Me H 58 H H H Me 5 H H H H 5	1092
	80°	 (85) + furan	1093
	160°	 (72) + CP	1093
	>112° in solution	 Ar (%) Ph 55 *p*-tolyl 60 *p*-ClC_6H_4 58 3,5-$Cl_2C_6H_3$ 83 + CP	1094
 Ar = same as preceding entry	110 -140° k_{endo}/k_{exo} = *ca.* 2	 (50 - 60) + CP	1095
	distill, 170°, 25 Torr	 (—)	1096
	625 - 650°, vacuum	 (80) + CP	1059
	FVP, 500°	 (≥ 75) + $C_{10}H_{14}$	509
	FVP, 500°	 R[1] R[2] (%) H H 100 Me H — Me Me — + $C_{10}H_{14}$	1097
	FVP, 500°	 (—) + $C_{10}H_{14}$	1098

[a] See reference 313, Table II for details of reaction conditions and products.

[b] See Mechanism section for other substituent k_{rel} values.

[c] Excess acrylonitrile was employed to achieve decarbonylation.

[d] The reaction was examined in the DA direction only; ca. 5% of the adduct formed.

[e] See Mechanism section for other substituent k_{rel} values.

[f] *Syn/anti* diastereomer ratios were determined for the products.

[g] The *cis* and *trans* isomers were run separately.

[h] The reaction was studied in the DA direction.

[i] The rDA details are not clear in the abstract (Japanese Patent).

[j] The stereochemistry of the starting material is unknown.

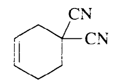
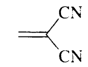
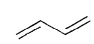
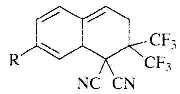
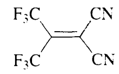
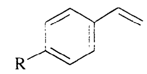
[k] Crossover experiments indicate that the process is r[3 + 3], not rDA.

[l] The structure of this material, a tarry residue, was not confirmed.

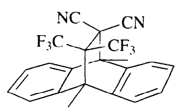
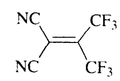
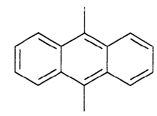
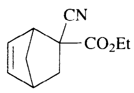
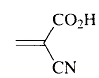
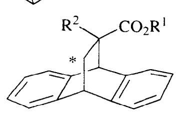
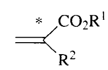
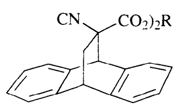
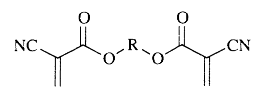
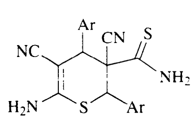
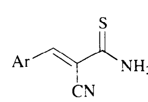
[m] This product is isolable at 78°.

[n] See Mechanism section for k_{rel}.

TABLE XI-A. 1,1-Di-EWG SUBSTITUTED ALKENES

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	brass tube, red heat	 (12) + 	1099
	25°, PhH, ⇌	 + 	1100

R	$10^3k_{DA}(M^{-1}s^{-1})$	$10^3k_{rDA}(M^{-1}s^{-1})$	$1/K_{eq}(M^{-1})$
t-Bu	31	1.6	19
Me	26	1.4	18
H	2.4	0.50	4.9
F	1.9	1.4	1.4
Cl	0.60	0.54	1.1
Br	0.41	0.42	0.98

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	150°	 +  (—)	443
	700°, 0.7 Torr (SO_2)	 (—) + CP	1101
 + MA; R[1] = Et, R[2] = CO_2Et; R[1] = i-Bu, R[2] = CN; * = ^{14}C	heat, mineral oil	 (—) + $C_{10}H_{14}$-MA	1102
 + MA; R = various linkers, e.g. $(CH_2)_n$ 19 examples	135°	 (16 - 100) + $C_{10}H_{14}$-MA	1102
	⇌		1103

Ar	K_{eq}(23°)
Ph	0.244
p-FC_6H_4	0.113
p-ClC_6H_4	0.078
p-BrC_6H_4	0.089
p-$O_2NC_6H_4$	0.0071
m-$MeOC_6H_4$	0.265
m-$O_2NC_6H_4$	0.010

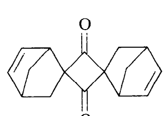
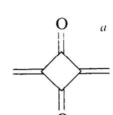
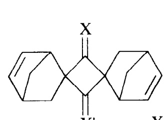
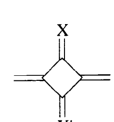
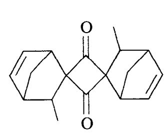
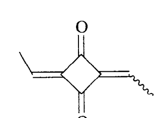
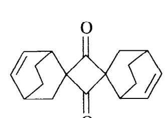
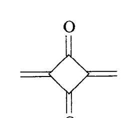
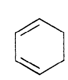
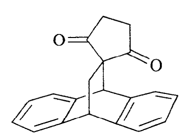
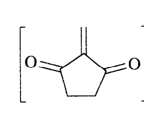
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 650°	 [a] (60) + CP	1104
 X &/or X' = O	FVP, 680° ⇌ −50°	 (—) + CP	857
	FVP, 680° ⇌ 25°	 (—) + CP	857
	FVP, 680° ⇌ −50°	 (—) + 	857
	TFA, catalyst	 (—) + $C_{10}H_{14}$	202

TABLE XI-A. 1,1-Di-EWG SUBSTITUTED ALKENES *(Continued)*

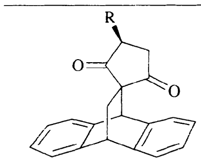
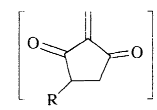
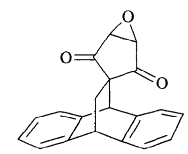
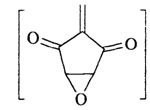
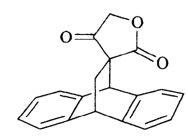
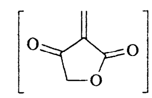
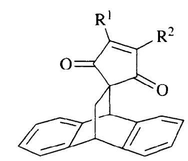
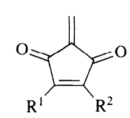
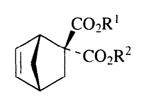
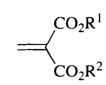
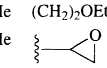
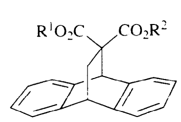
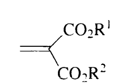
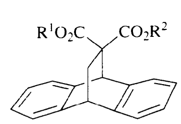
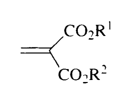
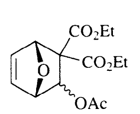
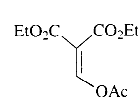
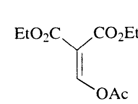
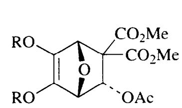
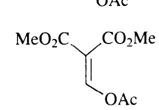
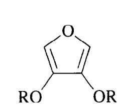
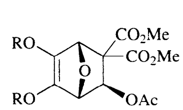
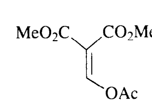
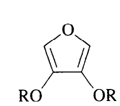
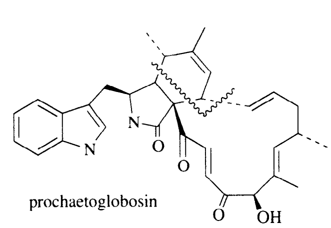
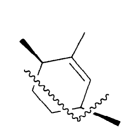
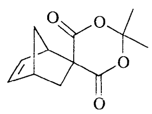
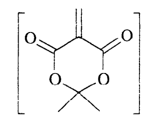
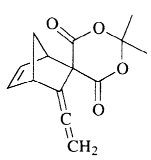
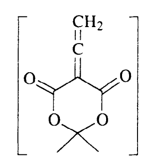
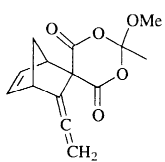
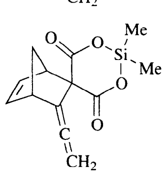
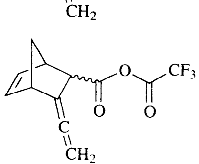
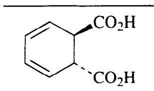
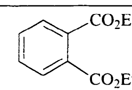
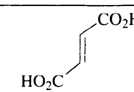
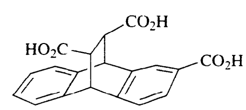
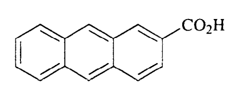
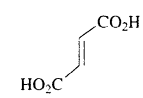
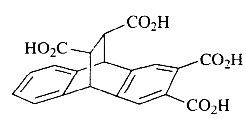
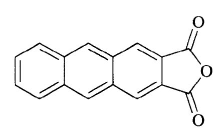
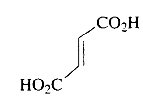
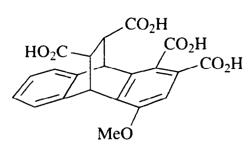
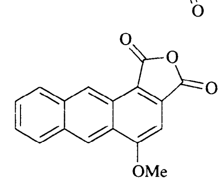
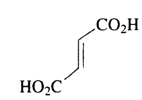
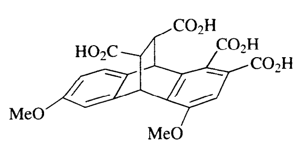
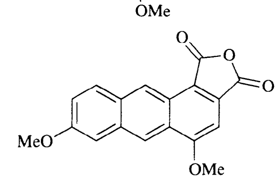
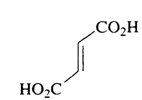
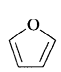
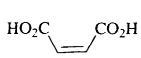
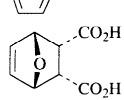
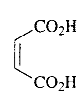
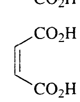
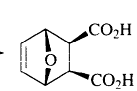
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	rt, silica gel, catalyst	 R (%): H 60; Me 62 + $C_{10}H_{14}$	187
	rt, silica gel, catalyst	 (—) + $C_{10}H_{14}$	187
	rt, silica gel, catalyst	 (—) + $C_{10}H_{14}$	187
	FVP	 (100) + $C_{10}H_{14}$	187
	625 - 650°, vacuum	 + CP R¹ R² (%): Me Me 80 Me Et 71 Me *n*-Bu 80 Et Et 65 Me allyl 80 Me $(CH_2)_2OEt$ 80 Me  65	1059
 + MA R¹, R² = alkyl, alkenyl, etc.	225°, mineral oil	 (20 - 81) + $C_{10}H_{14}$-MA	263
 + MA	220°	 + $C_{10}H_{14}$-MA R¹ R² (%): Et Et 60 allyl allyl 51 Et C_6H_{11} 52	264
	71.2° $k_{exo} = 2.9 \times 10^{-5}\ s^{-1}$ $k_{endo} = 6.1 \times 10^{-5}\ s^{-1}$	 (—) + furan	214
	rt, ZnI_2, catalyst	 (—) + furan	214
 R = Me or Bu	40°, silica gel	 (—) + 	186, 185
 R = Me or Bu	≥ 80°, silica gel	 (—) + 	186, 185
 prochaetoglobosin	180°, 5 h	 (45)	1105

TABLE XI-A. 1,1-Di-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 460 - 520°	 → $H_2C{=}C{=}C{=}O$ (—) + CP + CO_2 + acetone	1106, 1107
	550 - 650°	 → $H_2C{=}C{=}C{=}C{=}C{=}O$ (—) + CP + CO_2 + acetone	444
	350 - 500°	$H_2C{=}C{=}C{=}C{=}C{=}O$ (—) + CP + CO_2	444
	500°	$H_2C{=}C{=}C{=}C{=}C{=}O$ (—) + CP + CO_2	444
	450 - 725°	$H_2C{=}C{=}C{=}C{=}C{=}O$ (—) + CP	444

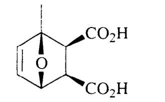
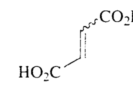
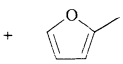
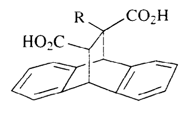
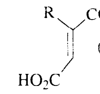
[a] This product polymerizes at rt.

TABLE XI-B. ACYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES

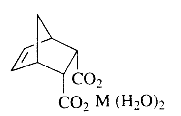
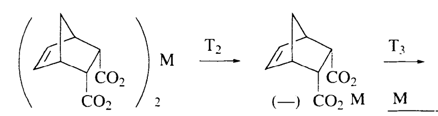
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + EtO_2C—≡—CO_2Et	220°	 (—) +  (—)	132
	259°	 (84) + 	1108
	259°	 (79) + 	1108
	259°	 (90) + 	1108
	259°	 (94) + 	1108
 + 	H_2O →	adduct —heat to melt→ adduct (higher mp) + furan	1109
	evaporation of solvent, or extraction	0.88/1 0.42/1  + furan	138
	H_2O, 28° ⇌	 + furan ⇌  Time / *endo*/*exo*[a]: 0 h 5/1; 165 h 0.88/1; 285 h 0.42/1	445

Time	*endo*/*exo*[a]
0 h	5/1
165 h	0.88/1
285 h	0.42/1

TABLE XI-B. ACYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2O	 (—) + 	1110
	142° [c] ⇄	 (—) + $C_{10}H_{14}$	477

R	10^2K_{eq}(M)	$10^7k_{rDA}(s^{-1})$
H	0.058	13.6
Me	13.7	21.4
Et	39.2	30
n-Pr	58.1	26.9
i-Pr	62.1	ND
n-Bu	62.1	29.4
i-Bu	263	ND
c-C_5H_9	32.5	ND
c-$C_6H_{11}CH_2$	164	ND
c-$C_6H_{11}(CH_2)_2$	65	ND

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat, T_1	 M + CP	1111

M	T_1	T_2	T_3
Fe^{+3}	147	290	390
Co^{+2}	242	330	395
Ni^{+2}	220	320	392
Cu^{+2}	160	218	300
Zn^{+2}	140	295	392

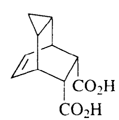
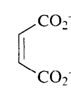
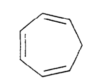
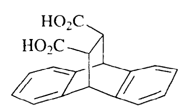
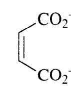
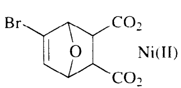
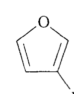
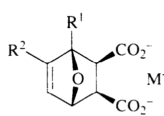
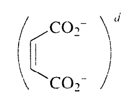
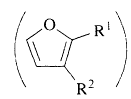
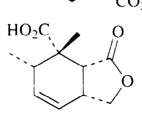
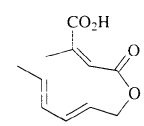
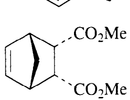
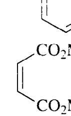
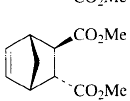
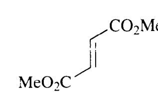
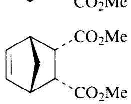
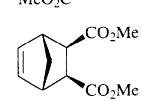
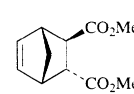
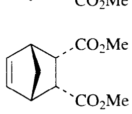
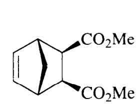
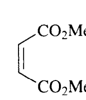
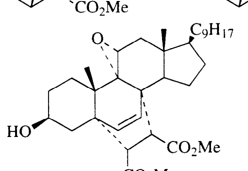
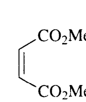
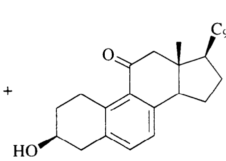
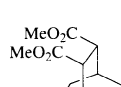
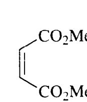
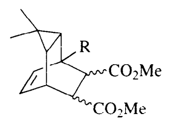
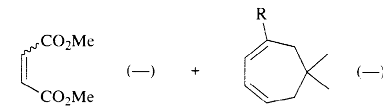
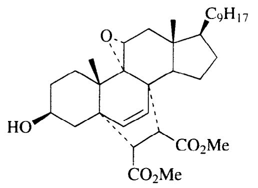
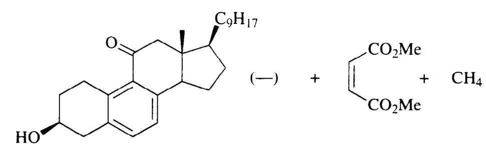
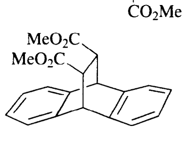
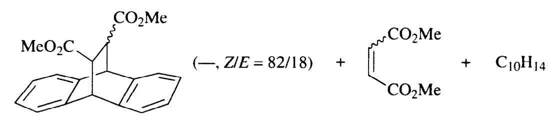
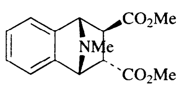
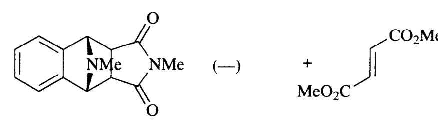
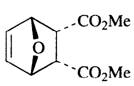
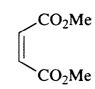
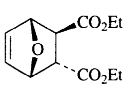
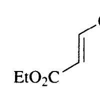
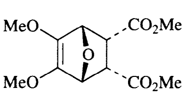
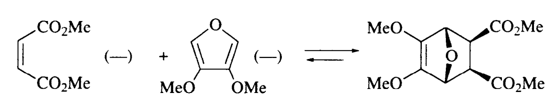
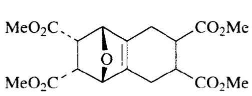
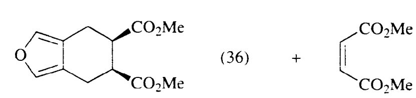
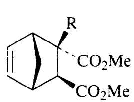
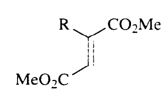
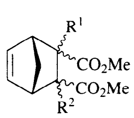
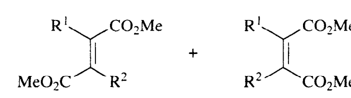
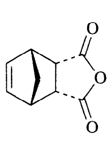
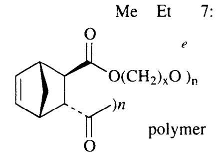
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cu_2O, 185°	 Cu(II) +  ("high")	1112
	Cu_2O, 185°	 Cu(II) + $C_{10}H_{14}$ ("high")	1112
	320°	 (91) + Ni(II)	1113
 R¹ R²: H H; Br H; H Br	140 - 345°, DTA	 + 	1114
	140 °, 15 h ⇄	 (—)	1115
	FVP, 500°	 (—) + CP	732
	FVP, 500°	 (—) + CP	732
	γ - alumina ⇄	 (—) +  (—)	188
 + 	alumina, rt	 (—) + CP	189
	260 - 280°	 +  (—) + CH_4	470
	$t_{1/2}$ (60°) = 6 h	 (—) + C_6H_6	284

TABLE XI-B. ACYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	250 - 270°	 (—) + (—)	762
	260 - 280°	 (—) + + CH_4	470
	UV	 (—, *Z/E* = 82/18) + + $C_{10}H_{14}$	1117
 + NMM	25°, $LiClO_4$/ether, 15 h; or 112°, $LiClO_4$/toluene, 12 h	 (—) +	220
	vacuum distillation	 (—) + furan (—)	445
	rt, 1 month (⇌)	 (—) + furan (—)	445
	rt (⇌)	 (—) + (—) ⇌	474
	150°, 1 h	 (36) +	557
	FVP, 650°	 R (%): Me 95; Et 90 + CP	1118
	FVP, 650°	 I + II + CP	1118
 + $HO(CH_2)_xOH$	heat	 [e] (—) polymer	1119

R^1	R^2	I:II	(%)
Me	Me	4:1	95
Et	Et	10:1	94
Me	Et	7:1	91

[a] Rapid cycloaddition in H_2O allowed isolation of *ca.* pure *endo* adduct "for first time".

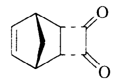
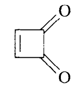
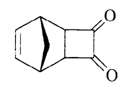
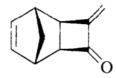
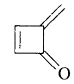
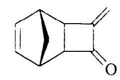
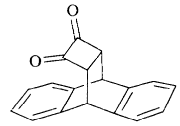
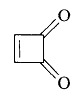
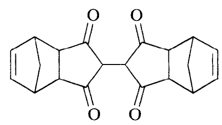
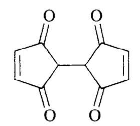
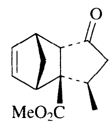
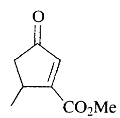
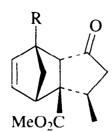
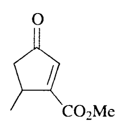
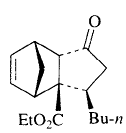
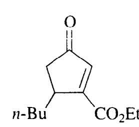
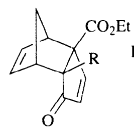
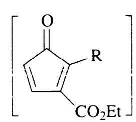
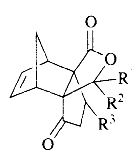
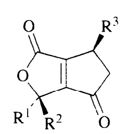
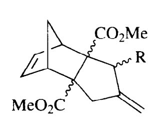
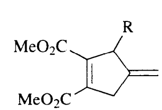
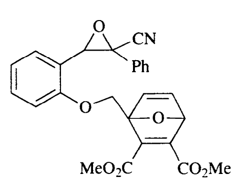
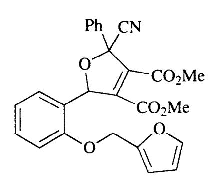
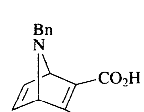
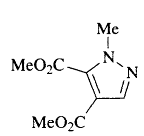
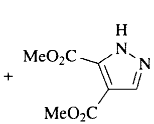
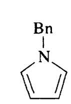
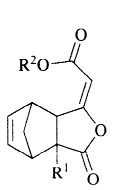
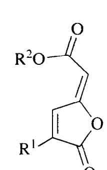
[b] Fumaric acid formed slowly, not via rDA pathway.

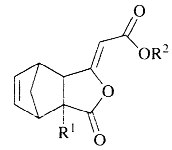
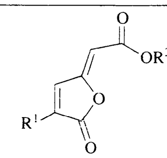
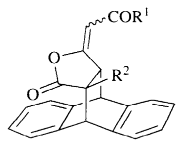
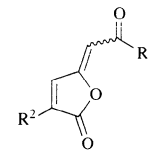
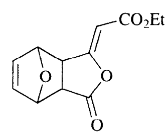
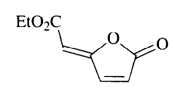
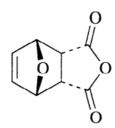
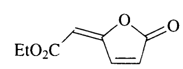
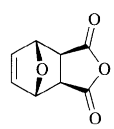
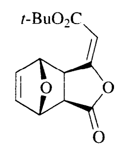
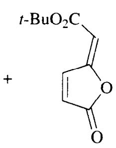
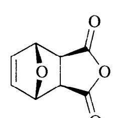
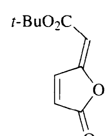
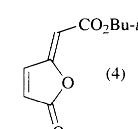
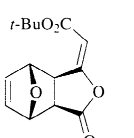
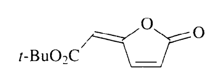
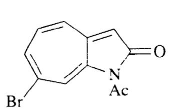
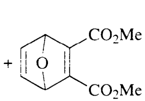
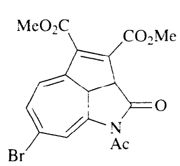
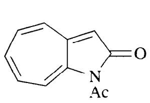
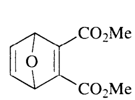
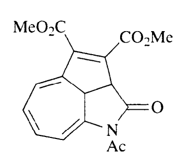
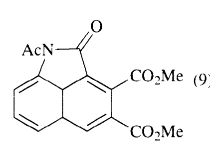
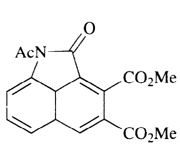
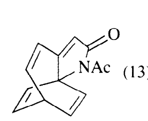
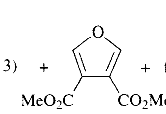
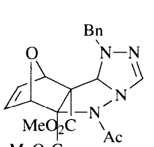
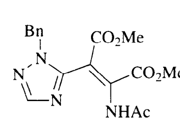
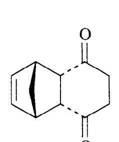
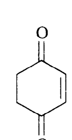
[c] The reaction was studied in the DA direction; values for rDA were calculated from K_{eq} and rate constants for DA reactions.

[d] The products were not analyzed.

[e] The partial *trans* structure was attributed to rDA, rearrangement, and DA reactions.

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES

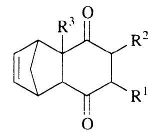
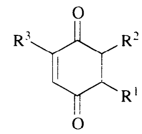
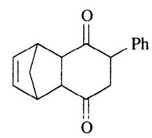
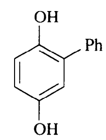
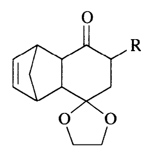
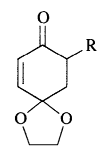
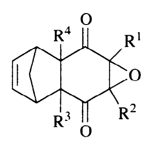
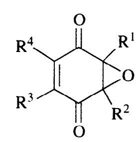
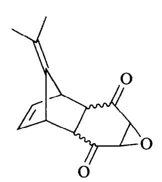
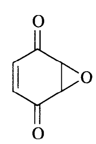
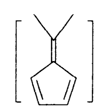
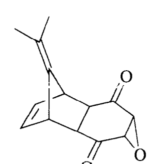
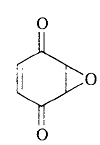
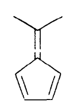
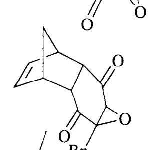
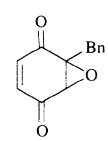
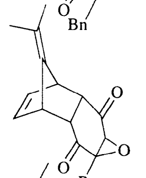
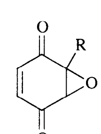
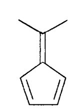
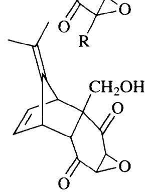
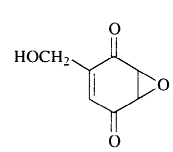
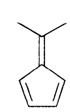
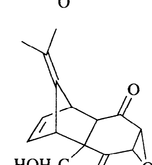
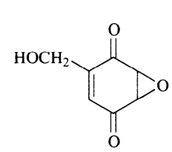
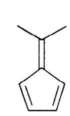
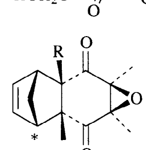
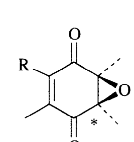
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	400°, 10^{-4} Torr	 (—) + CP $\xrightarrow{rt}$  *endo* + *exo*	449
	480°, 10^{-4} Torr	 (—) + CP $\xrightarrow{rt}$  *endo* + *exo*	449
	400 - 480°, vac.	 (15) + $C_{10}H_{14}$	449
	450°	 (60) + CP	450
	BF_3•Et_2O	 (10) + CP	208
	BF_3•Et_2O	 R / Temp / Time / (%): H / rt / 6 h / 95; Me / –10° / 6 h / 95 + CP(R)	217
 + MA	1.1 eq. $MeAlCl_2$, 70°, 1 h	 (82) + CP(MA)	208
 R = Me, Et, *n*-C_7H_{15}, allyl, or Bn	155°, DMF	 (—) + CP	1120
 R^1 / R^2 / R^3: H / H / Me; H / Ph / H, Me or Bu; Me / Me / H, Me or Bu	FVP, 520°	 (≥ 90) + CP	1121
	FVP, 530 - 550°	 R / (%): H / 100; Me / 94 + CP	808
	120°, $t_{1/2}$ = 5 h	 (86)	1122
 + CH_2N_2	20°, 2 d	 (54) +  (—) +  (98)	1123
 R^1 = H or Me; R^2 = Me, Et, or *t*-Bu	FVP, 450°	 (88 - 95) + CP	1124

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1 = H or Me, R^2 = Me, Et, or *t*-Bu	FVP, 450°	 (92-98) + CP	1124
	230°	 (see below) + $C_{10}H_{14}$ (90)	1125, 1126
	—	 (—) + furan	1127
 + $Ph_3\overset{+}{P}\overset{-}{C}HCO_2Et$	61°, $CHCl_3$	 (50) + furan	1128
 + $CHCO_2Bu$-*t* $=P(Ph)_3$	rt, 48 h	 (64) +  (26) + furan	453
 + $CHCO_2Bu$-*t* $=P(Ph)_3$	80°, 4 h	 (69) +  (4) + furan	453
	61°, 1 h	 (100) + furan	453
 + 	120°, 3 kbar	 (*ca.* 4) + furan	1129
 + 	120°, 3 kbar	 (6) +  (9) + furan	1130, 1131
	130°, 3 kbar	 (16) +  (13) +  + furan	1130, 1131
	100°	 (59) + furan	1132
	170°	 (≥ 40) + CP	452

Product yields for the 230° entry (refs. 1125, 1126):

	R^1	R^2	*E:Z*	(%)
E	H	H	1:1	80
Z	H	H	1:1	77
E,Z	Me	Me	—	23

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	175°, vacuum distill	 R^1 R^2 R^3 (%) H H H 45 Me Me H 52 Me Me H 44 (*trans*) Me H Me 65 Me Me Me 57 (*trans*) *t*-Bu H H 73 + CP	451
	175°, vacuum distill	 (—) + CP	451
	175°, vacuum distill	 R (%) Ph 85 Me "good" + CP	451
 R^1 R^2 R^3 R^4 H H H H Me H H H Me Me H H Me H Me H Me H H Me	420°, 10 Torr	 (—) + CP	1133
	150°	 (—) + 	1133
	180°, 40 min	 (100) + 	1001
	250 - 270°	 (94) + CP	1134
	heat	 R Temp Time (%) H 160° 0.5 h 95 Me 150° 0.5 h 100 CH_2OH 165° 0.5 h 82 + 	1001, 1004
	140°	 (70) + 	1002
	140°	 (62) + 	1002
 R = phytyl	170°	 (90) + CP	1135

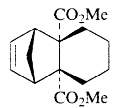
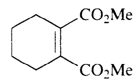
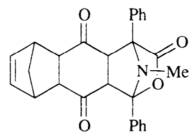
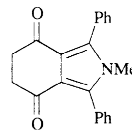
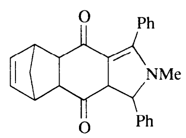
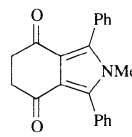
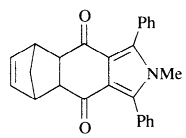
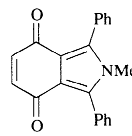
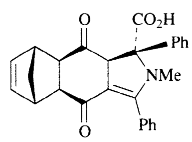
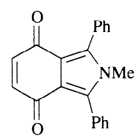
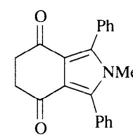
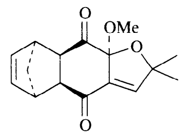
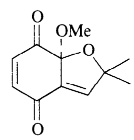
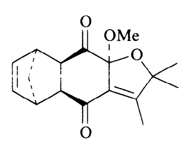
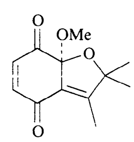
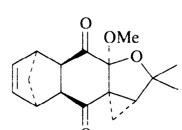
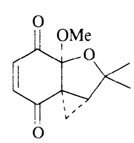
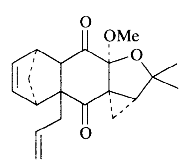
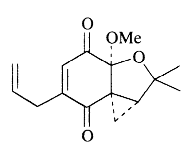
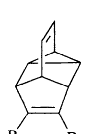
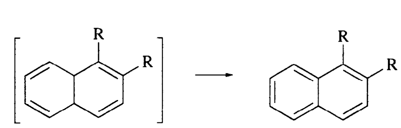
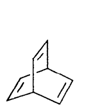
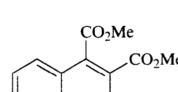
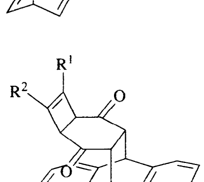
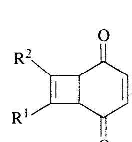
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 650°	 (92) + CP	1118
	140°	 I (74) + CP + CO_2	1136, 1137
	80°	I (74) + CP + CO_2	1138
	140°	 (—) + CP	1136, 1137
	138°	 (81) + CP	1138
	140°	 (34) +  (44) + CP	1139
	FVP, 400°	 (100) + CP	1140
	FVP, 425°	 (—) + CP	1140
	FVP, 400°	 (54) + CP	1140
	FVP, 545°	 (96) + CP	997
	heat (oxid.)	 R / Temp / (%): CN 100° 63; CO_2Me 150° 33	1141
 + DMAD	150° (oxid.)	 (12)	1141
	220°, 20 Torr	 R[1] R[2] (%): Me Me 98; H Ph 89 + $C_{10}H_{14}$	1142

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES *(Continued)*

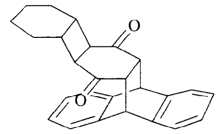
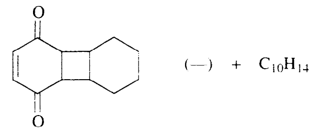
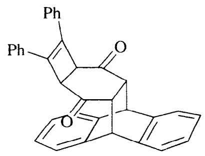
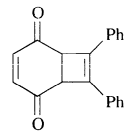
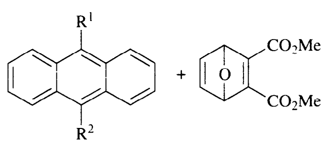
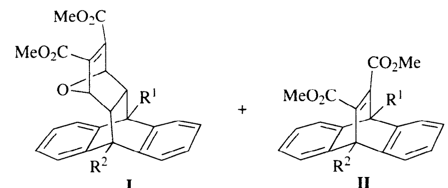
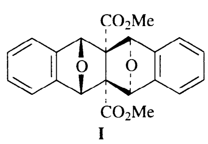
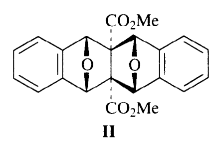
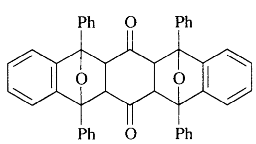
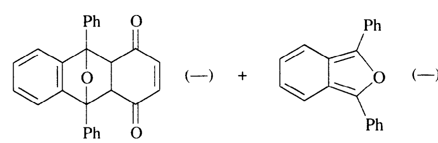
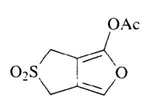
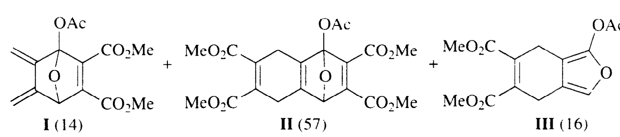
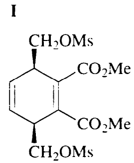
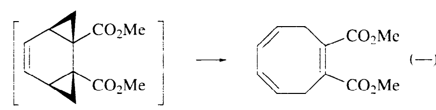
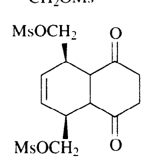
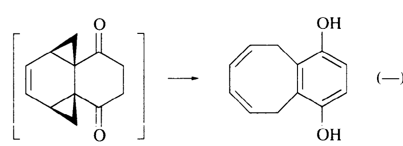
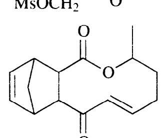
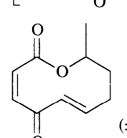
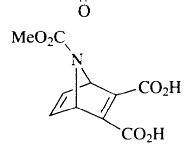
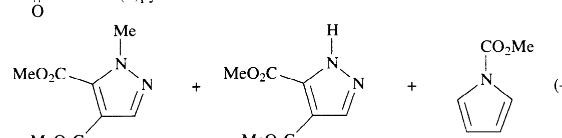
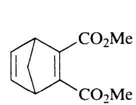
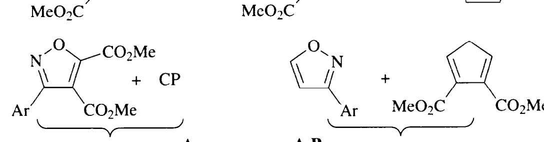
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	220°, 20 Torr	 (—) + $C_{10}H_{14}$	1142
	230 - 250°	 (71) + $C_{10}H_{14}$	1143
	140°, DMSO	 + furan R[1] / R[2] / I (%) / II (%) H / H / 64 / 19 H / Me / 64 / 26 Me / Me / 78 / 14	798, 799
 (I/II = 52/48)	140°, 396 h ⇌ 140°, 418 h	 (I/II = 68/32)	1072
	—		1144
 + DMAD	120°		454
I	120°, 6 h	II (36) + III (21)	454
	Li naphthalenide	 (—)	1145
	KOBu-*t*	 (—)	1145
	430°, vacuum	 (78) + CP (±)pyrenolide	1146
	1. CH_2N_2 2. 150 - 200°, vacuum	 (—)	241
 + ArCNO	120°	 Ar / A:B 4-$MeOC_6H_4$ / 11:89 Ph / 14:86 4-$NO_2C_6H_4$ / 4:96	455

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES (*Continued*)

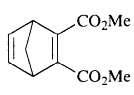
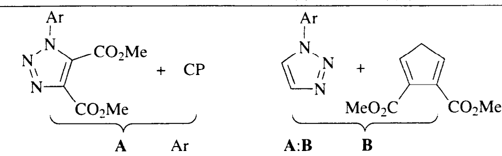
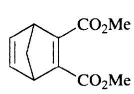
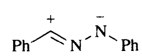
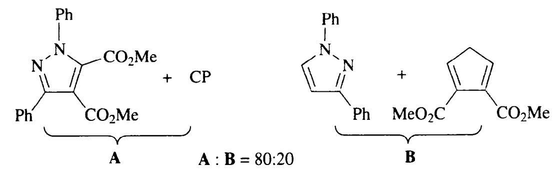
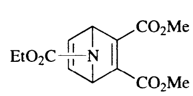
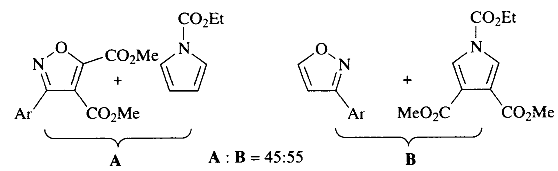
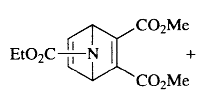
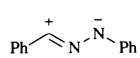
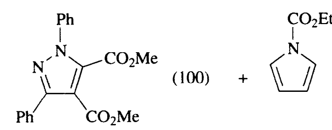
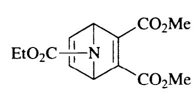
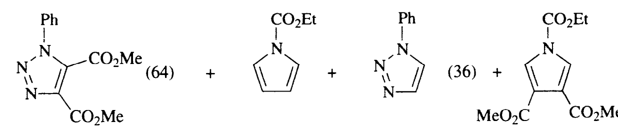
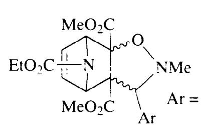
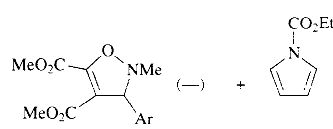
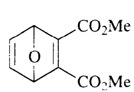
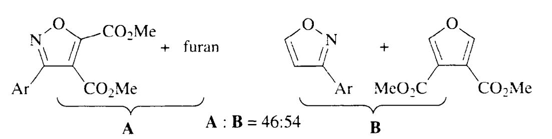
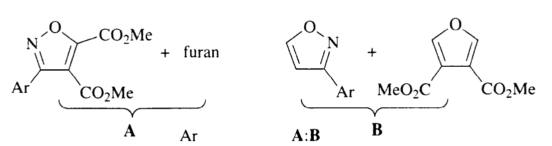
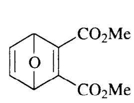
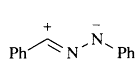
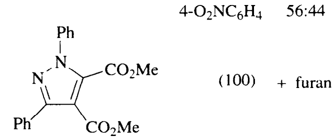
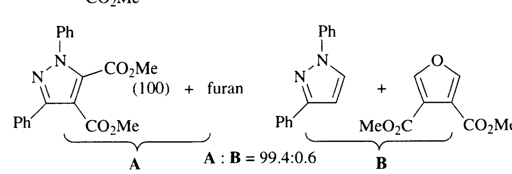
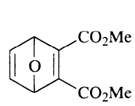
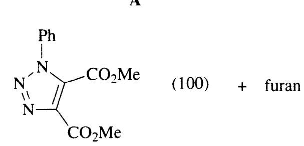
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + ArN_3	120°	 Ar / A:B 4-$MeOC_6H_4$ 23:77 Ph 23:77 4-$O_2NC_6H_4$ 9:91	455
 + 	120°	 A : B = 80:20	455
 + ArCNO Ar = mesityl	20°	 A : B = 45:55	1147
 + 	20°		1147
 + PhN_3	20°		1147, 1148
 Ar = Ph, or *p*-ClC_6H_4	150°		1148
 + ArCNO Ar = mesityl	—	 A : B = 46:54	1147, 1148
	120°	 Ar / A:B 4-$MeOC_6H_4$ 87:13 Ph 75:25 4-$O_2NC_6H_4$ 56:44	455
 + 	—		1147
	120°	 A : B = 99.4:0.6	455
 + PhN_3	—		1147, 1148

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES *(Continued)*

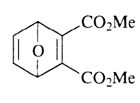
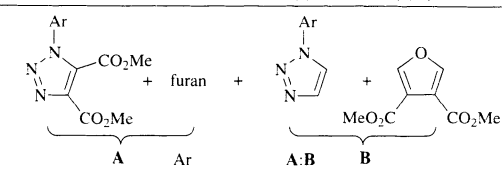
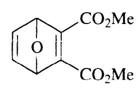
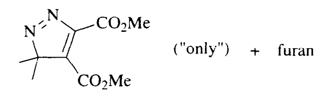
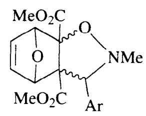
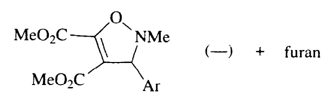
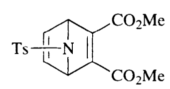
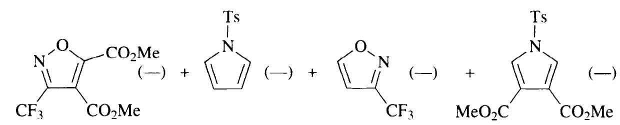
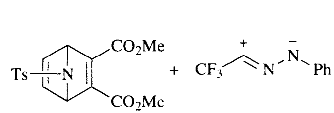
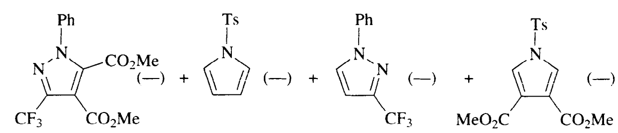
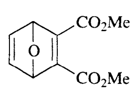
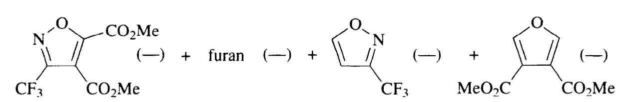
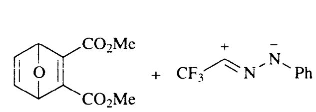
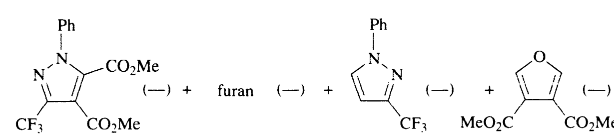
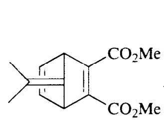
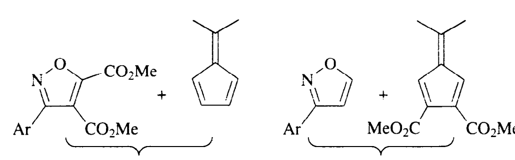
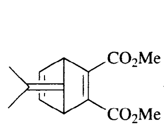
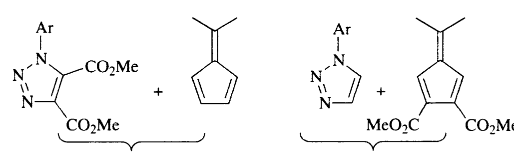
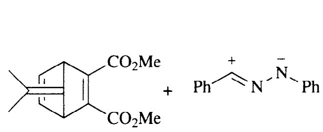
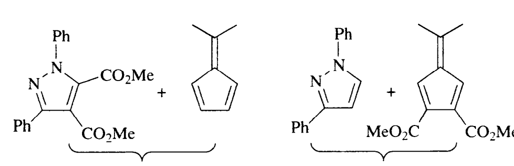
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + ArN_3	120°		455
		Ar / A:B: 4-$MeOC_6H_4$ 91:9; Ph 82:18; 4-$NO_2C_6H_4$ 52:48	
 + Me_2CN_2	120°		455
 Ar = Ph or *p*-ClC_6H_4	150°		1148
 + CF_3CNO	—		1149
	—		1149
 + CF_3CNO	—		1149
	—		1149
 + ArCNO	120°		455
		Ar / A:B: 4-$MeOC_6H_4$ 17:83; Ph 10:90; 4-$O_2NC_6H_4$ 52:48	
 + ArN_3	120°		455
		Ar / A:B: 4-$MeOC_6H_4$ 22:78; Ph 17:83; 4-$O_2NC_6H_4$ 6:94	
	120°		455
		A:B = 83:17	

TABLE XI-C. CYCLIC 1,2-Di-EWG SUBSTITUTED ALKENES (*Continued*)

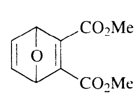
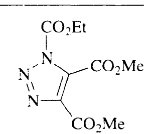
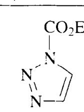
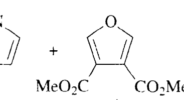
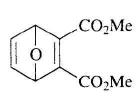
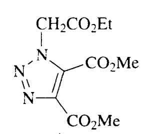
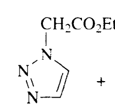
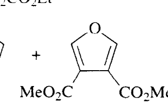
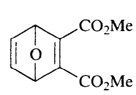
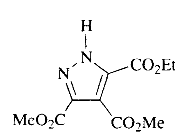
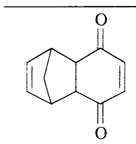
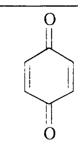
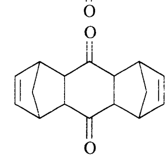
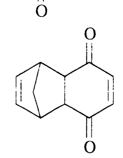
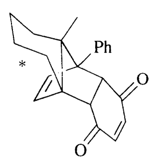
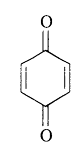
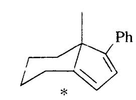
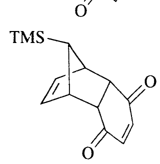
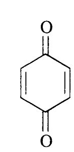
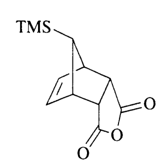
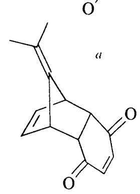
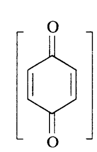
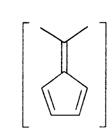
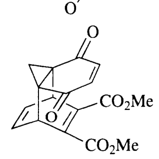
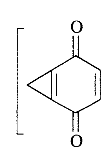
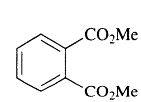
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + N_3CO_2Et	rt - 60°	 + furan  +  **A** **A**:**B** = 33:67 **B**	1150
 + $N_3CH_2CO_2Et$	rt	 (64) + furan  +  **A** **A**:**B** = 86:14 **B**	1150
 + N_2CHCO_2Et	rt	 (97) + furan	1150

TABLE XI-D. QUINONES AS DIENOPHILE

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	55 - 79° $E_a = 29$	 (—) + CP	259, 839, 1151
	49 - 79° $E_a = 27$	 (—) + CP	259, 839, 1151
	rt	 (—) + 	457
 + MA	58 - 78° $E_a = 25$	 +  (—)	258
 [a]	rt	 + 	456
	FVP, 500°	 (—) + 	459

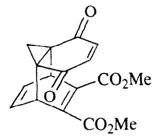
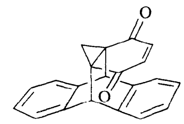
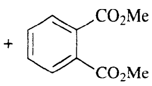
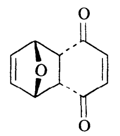
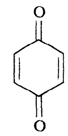
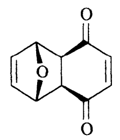
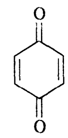
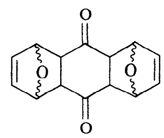
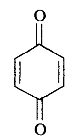
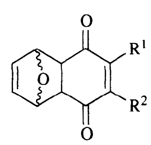
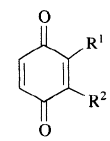
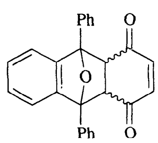
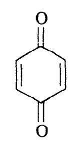
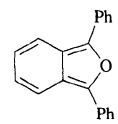
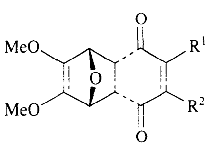
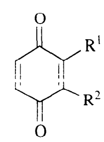
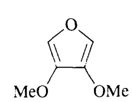
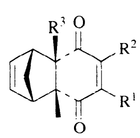
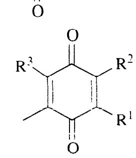
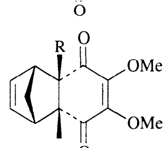
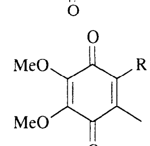
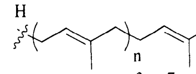
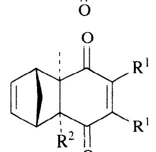
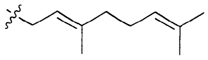
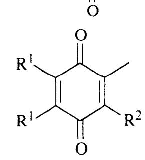
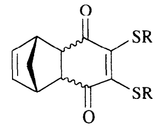
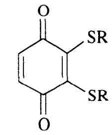
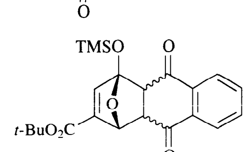
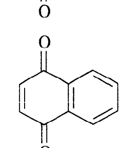
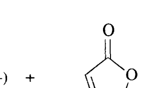
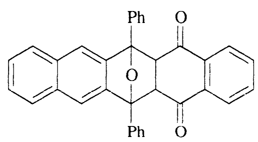
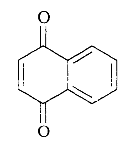
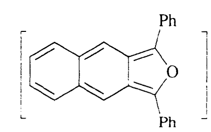
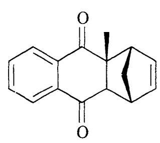
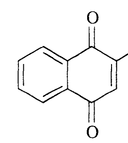
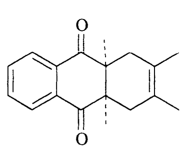
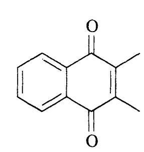
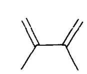
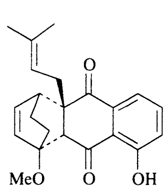
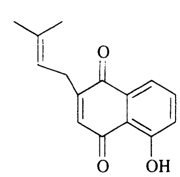
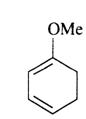
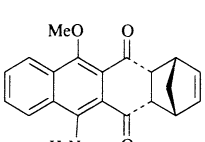
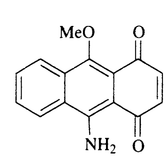
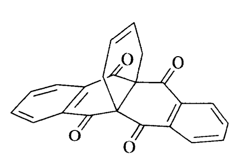
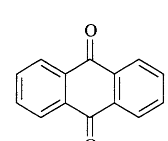
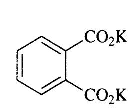
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + $C_{10}H_{14}$	heat	 (12) +  (16)	459
	–8°, 1 h, 1 atm	 (100) + furan	458
	5°,12 h, 1 atm	 (100) + furan	458
	≤ rt, 1 atm	 (—) + furan	458
 R^1 R^2: Me H; OMe OMe	≤ rt, 1 atm	 (—) + furan	458
	rt, solution ⇌	 (—) + 	475
	26 - 52°, 1 atm	 +  R^1, R^2, E_a: H, H, 24.5; H, Me, 25.9; OMe, OMe, 27.2	1152, 1153
	115°	 R^1, R^2 / R^3 / (%): H, OMe / phytyl-CO_2Me / —; benzo / phytyl-CO_2Me / 85 + CP	1154
	heat	 R / Temp / (%): H / 170° / 30;  n = 3 or 7 / 110° / — + CP	1155
 R^1 = OMe, OMe; —O(CH_2CH_2O)$_3$—; or —O(CH_2CH_2O)$_4$— R_2 = 	80°	 (100) + CP	1156
	180°, 0.2 Torr	 R (%): Me 88; Et 77; *n*-Bu 80 + CP	1157
	H_3O^+, rt	 (—) +  (—)	205

TABLE XI-D. QUINONES AS DIENOPHILE (*Continued*)

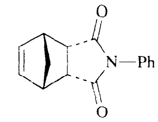
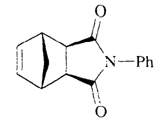
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	80° ⇌ cool	 (—) + 	1158
	90°, solvent	 (—) + CP	1159
	vacuum distill	 (—) + 	1160
	190 - 210°	 (94) + 	1161
	112°	 (75) + CP	1162, 1163
	aq. KOH (air oxidation)	 (—) + 	255

Solvent	AN*	$10^4k(s^{-1})$
hexane		1.94
cyclohexane	0	2.24
benzene	8.2	4.68
EtOAc	9.3	4.5
dioxane	10.8	6.0
acetone	12.5	5.7
DMF	16.7	8.6
1,2-$Cl_2C_2H_4$	16.7	7.8
MeCN	18.9	8.2
DMSO	19.3	11.2
$CHCl_3$	23.1	8.5
t-BuOH	27.1	10.0
i-PrOH	33.8	12.2
EtOH	37.9	13.3
MeOH	41.3	15.9
HOAc	50.0	24.9

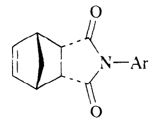
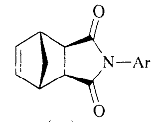
*AN = acceptor number

[a] The *endo* isomer is unstable at rt, even in the solid state. In contrast, the *exo* isomer is stable.

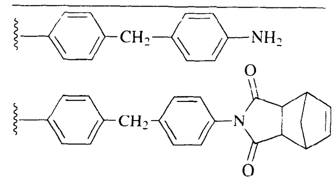
TABLE XI-E. MALEIMIDES

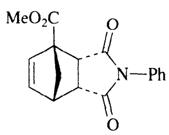
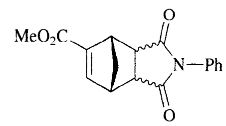
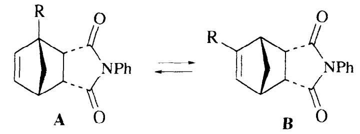
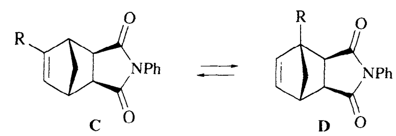
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat, solvent		1164, 1165

Temp	Time	Solvent	exo (%)
200°	12 h	none	25
200°	6 h	cymene	6
200°	12 h	cymene	48
200°	12 h	C_6H_5Cl	61
200°	6 h	$(Ph)_2CH_2$	53
200°	12 h	$(Ph)_2CH_2$	82
250°	4 h	$(Ph)_2CH_2$	90

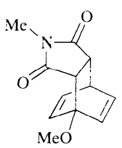
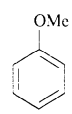
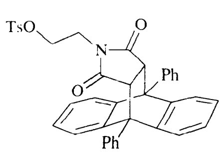
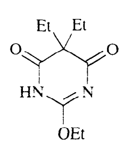
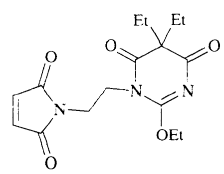
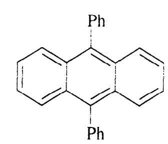
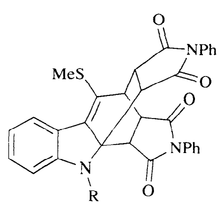
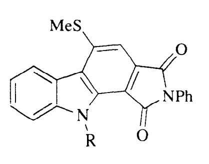
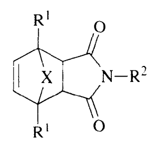
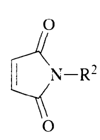
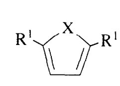
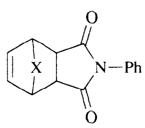
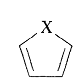
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	≥ 210°	 (—)	1166

Ar



Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	200°	 (90)	378
	200°, 15 h		1167

R	A (%)	B (%)	C (%)	D (%)
H	44	*endo*	56	*exo*
Ph	1	37	62	tr
CO_2Me	2	27	71	1

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	20°; $t_{1/2}$ *ca.* 0.5 h	NMM (—) +  (—)	285
 + 	210°	 (21) + 	1168
	150° (oxidation)	NPM +  (—)	1169
 R^1 = alkyl, R^2 = alkyl or aryl, X = $(CH_2)_n$, NH, NEt, N-allyl, or O	≥ 200°	 (80 - 100) + 	266
	≤ 70°	NPM + 	1170

	X	E_a	log A	$\Delta V^{\#}$
endo	NCOPh	24.1	13.2	−8.3 cm^3/mol
exo	NCOPh	31.5	15.3	—
exo	NCOMe	28.2	14.3	—
—	O	20.0	9.5	—

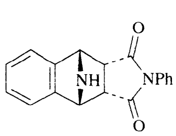
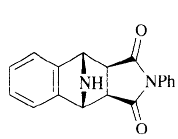
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	138°	 (—)	1171

TABLE XI-E. MALEIMIDES (*Continued*)

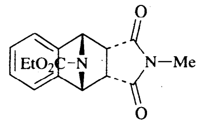
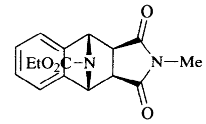
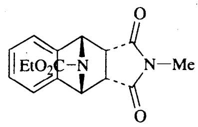
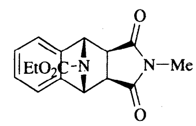
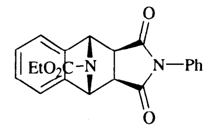
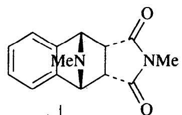
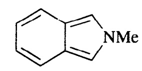
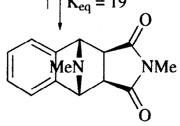
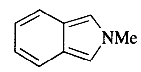
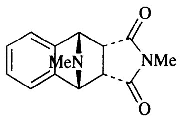
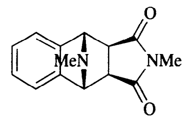
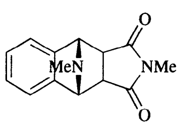
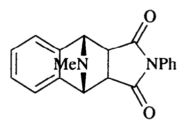
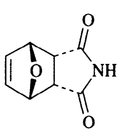
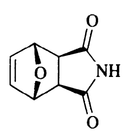
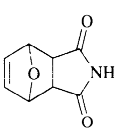
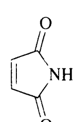
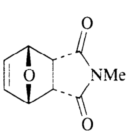
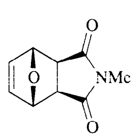
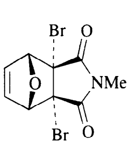
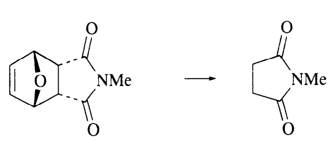
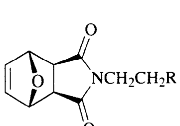
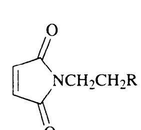
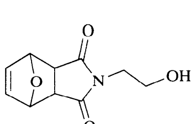
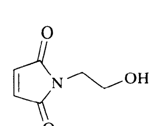
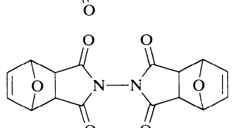
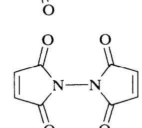
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + NMM	145°, 18 h	 (44)	1172
 + NPM	145°, 16 h	 (23) +  (20)	1172
	61°; $\Delta G^{\#} = 24.3$	[NMM + ] → adducts	220
↑↓ $K_{eq} = 19$			
	61°; $\Delta G^{\#} = 28.9$	[NMM + ] → adducts	220
	25°, $LiClO_4$/ ether ⇄		220
 + NPM	$LiClO_4$ / ether K_{eq} = *ca.* 1 ⇄	 + NMM	220
	80°, 15 min ⇄		1173
	180 - 190°	 (77) + furan	461
	40°, CD_3CN; $\Delta G° = -1.8$ ⇄		267
	Zn•Ag, THF or MeOH [a] $ZnBr_2$, reflux 4 h	 (—) + furan	1174
	157°	 R — (%) Cl — 59 Br — 75 9-adenine — 89 1-thymine — 82 1-cytosine — 95 9-(6-chloro)purine — 74 + furan	1175
	180°	 (80) + furan	462
	149 - 203°	 (87) + furan	463, 1176, 1177

TABLE XI-E. MALEIMIDES (*Continued*)

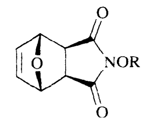
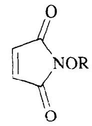
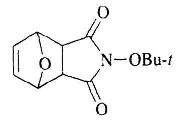
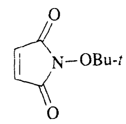
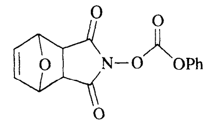
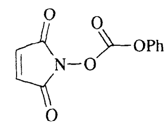
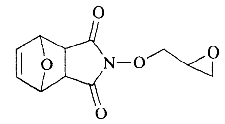
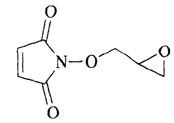
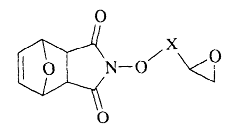
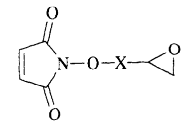
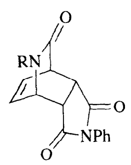
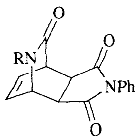
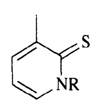
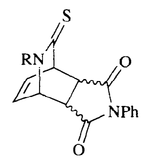
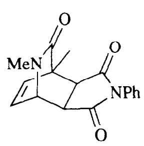
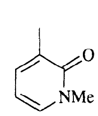
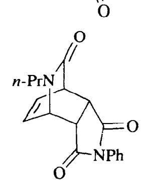
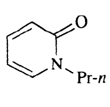
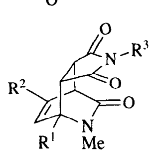
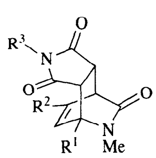
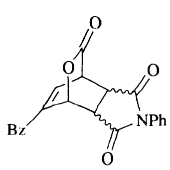
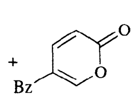
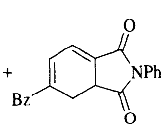
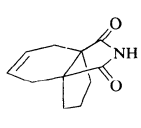
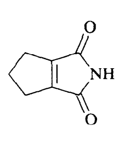
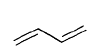
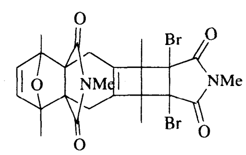
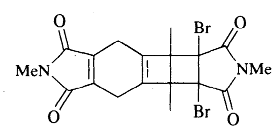
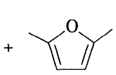
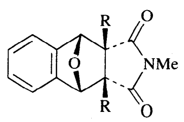
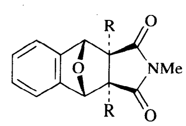
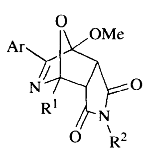
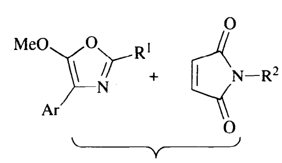
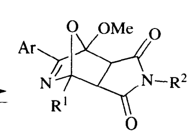
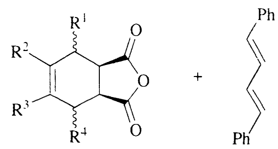
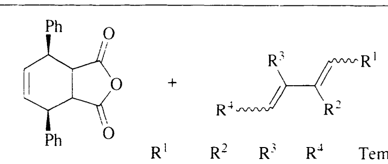
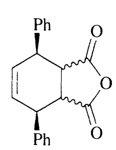
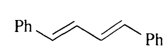
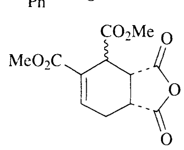
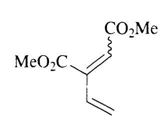
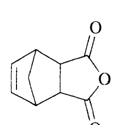
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140 - 190°	 R (%): Bn 93; Ac 94; Bz 94; $PhSO_2$ 90; Me 80 + furan	1178
	150°, vacuum	 (75) + furan	1179
	160°	 (78) + furan	1180
	138°, N_2 stream	 (64) + furan	1181
 X = $(CH_2)_nOCH_2$, $C_6H_4ZCH_2$, or $(CH_2)_{n+1}SCH_2$; Z = O or S; $n \geq 0$	138°, N_2 stream	 (—) + furan	1181
 R = Me, Et, or Pr	140 - 160°	 (—)	1182
 + NPM; R = Me, Et, or Pr	heat	 (—) Temp / Isomer: 80 - 110° *endo*; 140° *endo + exo*; 180° decomposition	1182
	225 - 240°	NPM (84) +  (—)	1183
	165 - 180°	NPM (91) +  (—)	1183
 R^1 R^2 R^3: H H H or Ph; H Me H or Ph; Me H H or Ph	≥ 130 ° ⇌	 (—)	1184
	140°	NPM +  (—) +  (15) + CO_2	464
	FVP, 600°	 (60) + 	465

TABLE XI-E. MALEIMIDES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP	 (—) + 	739
	132° ⇌	 R | ΔG° | k_{exo} H | −2.4 | $0.95 \times 10^{-8}\ s^{-1}$ Cl | −3.1 | $36 \times 10^{-8}\ s^{-1}$ $(CH_2)_4$ | −1.5 | $40 \times 10^{-8}\ s^{-1}$	267
 **A** R^1 = Me or Et R^2 = Me, Et, or Ph Ar = $4\text{-}O_2NC_6H_4$	80° ⇌	 **B** ⇌  **C** R^1 | R^2 | **A**:**B**:**C** Me | Et | 20:40:40	1185

[a] The *exo* isomer does not give the succinimide under these conditions.

TABLE XI-F. MALEIC ANHYDRIDE

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	heat	 (see below)	268
	heat, 15 Torr	 + MA	1186
 *cis* : *trans* = 1:1	rt, silica gel ⇄ 110°	 (—, *E* : *Z* = 1:1) + MA	184
	heat ⇄	MA + CP (—)	132

R^1	R^2	R^3	R^4	Temp	(%)
t-Me	H	H	H	350°	7
c-Me	H	H	H	360°	—
c-Pr	H	H	H	360°	—
t-Et	H	H	H	330°	14
t-Pr	H	H	H	330°	5
t-(*t*-Bu)	H	H	H	350°	7
t-Me	H	H	*t*-Me	310°	35 (*E,E*)
t-Et	H	H	*t*-Me	310°	30 (*E,E*)
c-Me	H	H	*t*-Me	350°	8
c-Me	H	H	*t*-Et	350°	6
H	Me	Me	H	310°	20

t = trans; *c* = cis

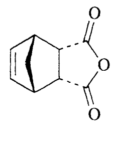
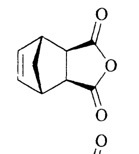
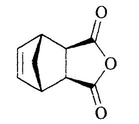
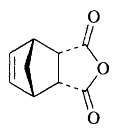
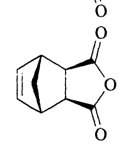
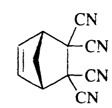
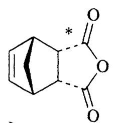
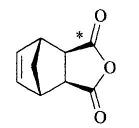
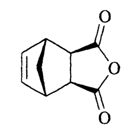
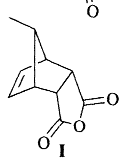
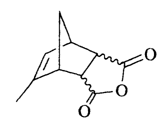
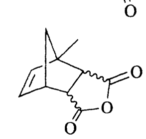
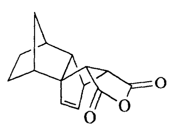
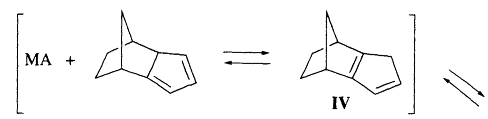
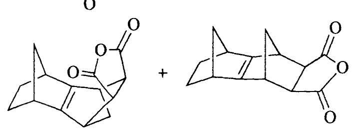
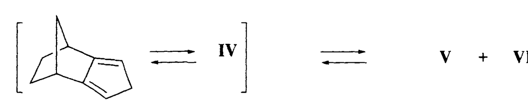
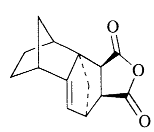
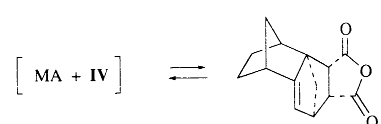
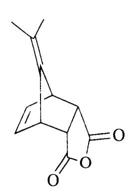
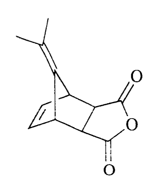
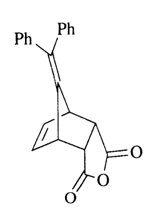
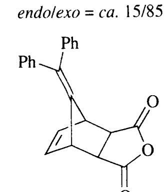
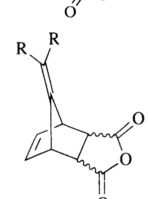
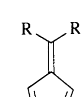
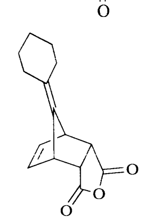
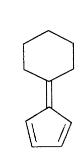
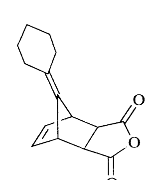
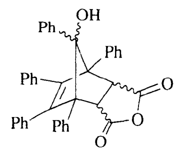
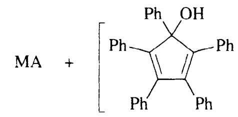
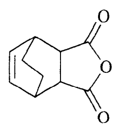
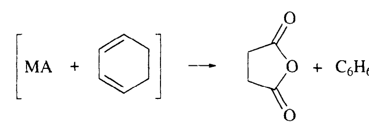
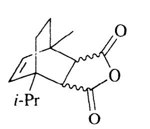
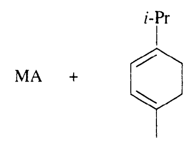
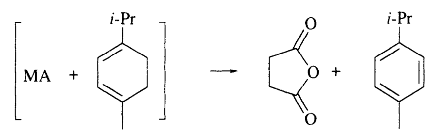
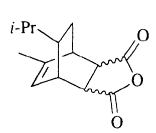
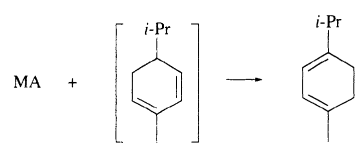
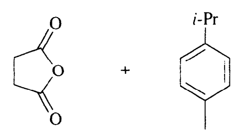
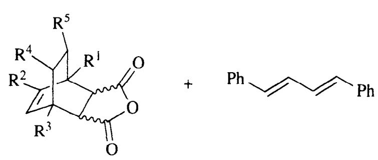
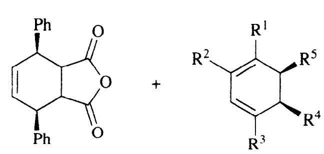
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	190°	 (—)	1187
	≥ 150°	 (—)	137
 + TCNE	heat, decalin	 (—) +  (—)	135
 * = ^{14}C	190°	 (—) +  (—)	134
 **I**	180 - 207°; E_a = 41.3 ⇌	 **II** +  **III** **I** /**II** /**III** = trace /1.0 /0.46	466, 467
	170°, 10 min ⇌		1188
	170°, 40 min ⇌		
 **V**	170°, 12 h ⇌ K_{eq} (**VI**/**V**) = 10	 **VI**	1188
	80°, 1 h	 (60 - 80)	1189, 1190
	80°	*endo*/*exo* = *ca.* 1/1	133
	80°	*endo*/*exo* = *ca.* 15/85	133
	heat, 135° ⇌	 (—)	601, 1191, 1190
 R, R: Ph, Ph; —(CH$_2$)$_4$—; —(CH$_2$)$_5$—	rt, dilute ⇌ concentrate	MA + 	1192, 1190
	heat ⇌	MA +  ⇌ 	1193

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	290 - 300°, 15 Torr	 (—)	865
	heat (⇌)		132
	250°	 (—)	1194
	flame heat	 (—)	468
	> 250°		1194
	flame heat	 (—)	468
	heat		268

R^1	R^2	R^3	R^4	R^5	Temp	Yield
H	H	H	H	H	325°	35
H	H	H	—(CH$_2$)—		260°	70
i-Pr	H	Me	H	H	300°	55
H	Me	H	*i*-Pr	H	310°	45
Me	Me	H	*i*-Pr	H	310°	50
Et	Me	H	*i*-Pr	H	310°	45

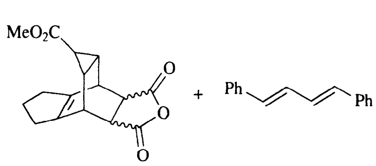
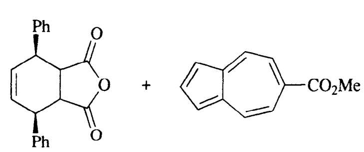
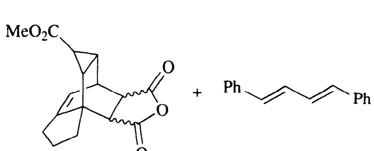
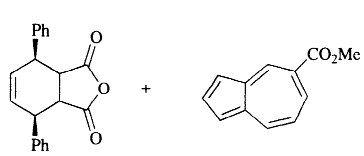
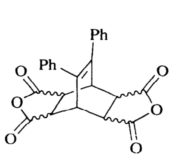
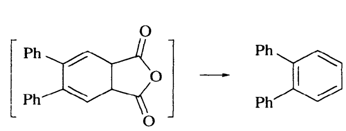
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	330 - 340°	 (—)	268a
	330 - 340°	 (—)	268a
	$Ba(OH)_2$, pyrolysis	 (18 - 50)	1195

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

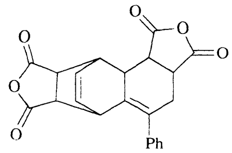
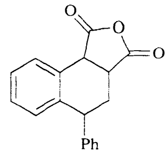
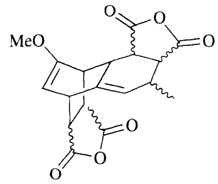
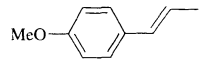
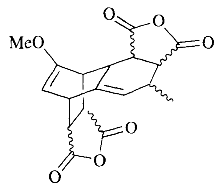
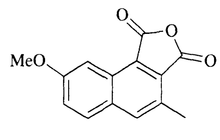
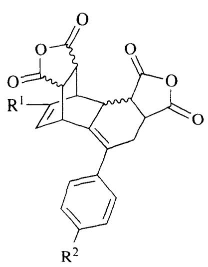
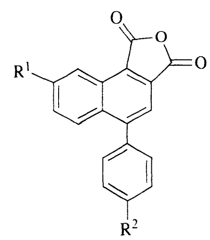
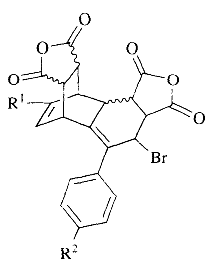
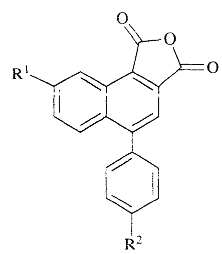
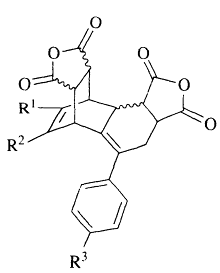
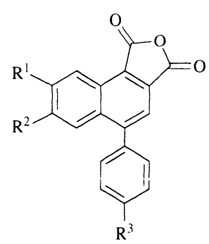
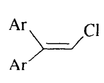
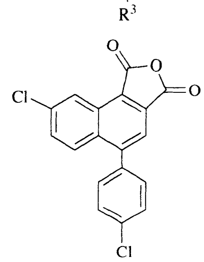
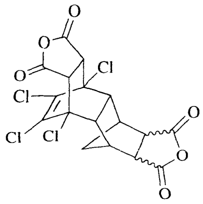
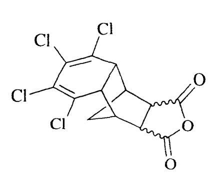
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	HI, P, HOAc, 115°	 (—) + MA	1196
	heat, vacuum	 anethole (—) + MA	469
	S_8, 235°	 (—) + MA	469
	S_8, 240 - 320°	 R[1] / R[2] / (%): H / Me / 88; H / Et / 75; H / *i*-Pr / low; H / *t*-Bu / 87; H / F / 50; H / Cl / 67; F / Me / 40; H / F / low; Me / Me / 100; Cl / Cl / 50 + MA	1197
	sublime	 R[1] / R[2] / (%): H / H / 38; OMe / OMe / 29; Br / H / 29; Ph / H / — + MA + HBr	1198
	S_8, 220 - 300°	 R[1] / R[2] / R[3] / (%): H / H / H / 65; OMe / H / H / 60; OMe / H / OMe / 60; OMe / OMe / H / 60; Ph / H / H / 70; H / H / Me / 64 + MA	1199
 + MA Ar = *p*-chlorophenyl	180°	 (46) + MA	1200
	320°	 (—) + MA	1201

TABLE XI-F. MALEIC ANHYDRIDE *(Continued)*

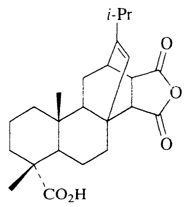
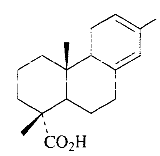
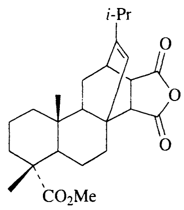
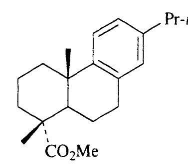
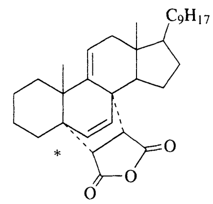
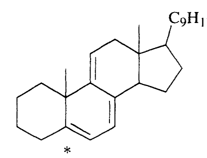
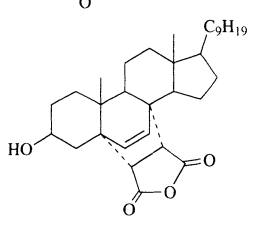
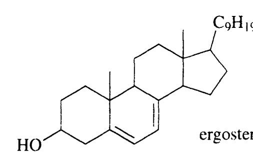
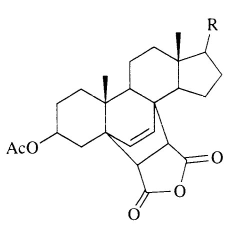
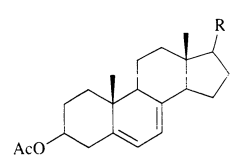
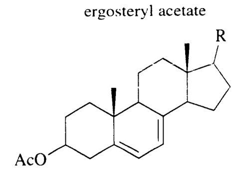
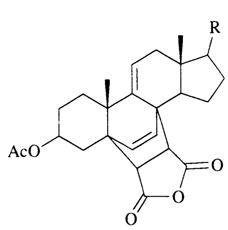
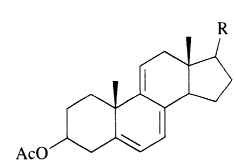
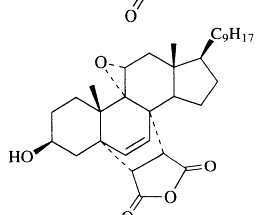
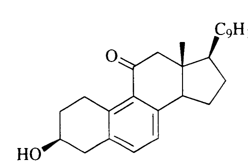
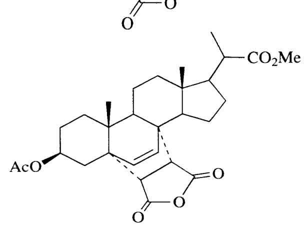
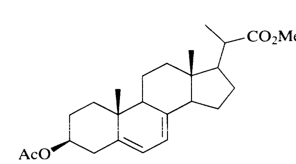
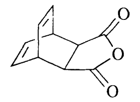
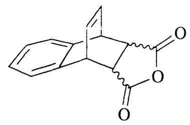
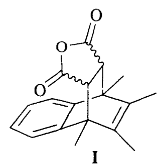
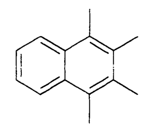
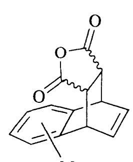
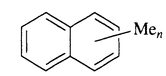
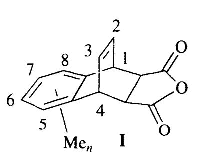
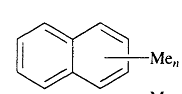
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	310°	 (—) + MA	694
	Se, 250°	 (60) + MA	1202
	240°, 12 Torr	 (60) + MA	1203
	220°	 (100) + MA ergosterol	1204
	heat	 (—) + MA ergosteryl acetate	1205
	220°	 (—) + MA	1206
	distill	 (—) + MA dehydroergosteryl acetate	1207
	260 - 280°	 (50) + MA + CH_4	470, 1208, 1209
	280°, 30 Torr	 (30) + MA	1208

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	$t_{1/2}$ (25°) = *ca.* 30 h	MA + C_6H_6	279
	200°	MA + $C_{10}H_8$	1210
 (5%) I	138°; K_{eq} = *ca.* 20 ⇄	MA +  (95%) II	1211
I (*ca.* 90%)	80°, 30 equiv. MA ⇄	II (10%)	1211
	100°, 30 equiv. MA ⇄	MA + 	1212, 1213

Substituents	1 h (%)	3.5 h (%)	24 h (%)	48 h (%)	72 h (%)
none	—	—	<1	—	—
1-Me	—	—	<1	—	—
2-Me	—	—	14	11,13	—
1,2-Me_2	7.5	27	25,26	25	—
1,4-Me_2	—	6	12	11	—
2,3-Me_2	5.5	14,16	43,46	—	39
1,2,3,4-Me_4	74	93	ND	88	—
2,3-Et_2	9	25	41	38	—

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 I "*endo*" [a] + MA	155°, 6 h	 II + MA	1214, 1213

Me at C#	II (%)	I (%)	*exo/endo*
2,3	90	10	0.6
1,2,3,4	60	40	0.5
1,4,5,8	77	23	0.13
2,3,5,8*	86	14	1.0
1,2,3,4,5,8	0	100	0
1,2,3,4,6,7 &			
2,3,4,5,6,7,8 (4:3)	30	70	0.7-0.3
1,2,3,4,5,6,7,8	20	80	0.23

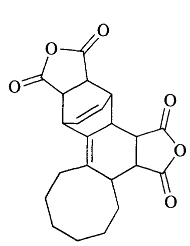
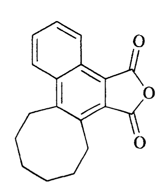
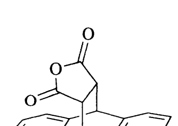
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	240°, S_8	 (54) + MA	1215
	flame heat	MA + $C_{14}H_{10}$ (—)	468
	heat, soda lime	MA + $C_{14}H_{10}$ (80)	1216
	400 - 430°, soda lime	MA + $C_{14}H_{10}$ (94)	1217

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

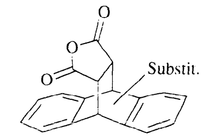
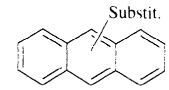
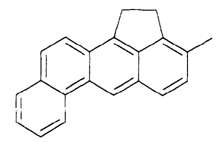
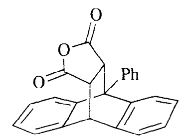
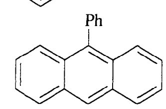
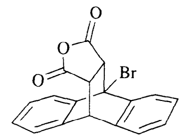
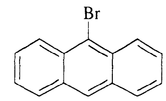
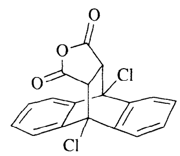
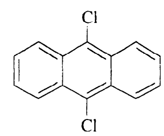
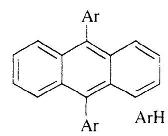
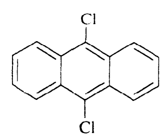
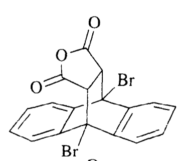
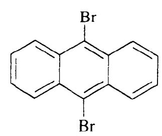
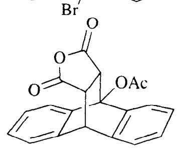
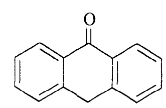
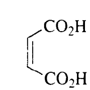
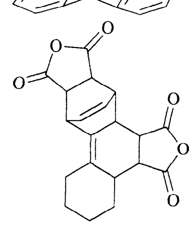
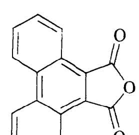
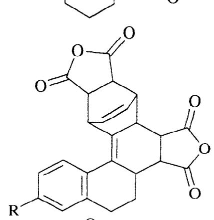
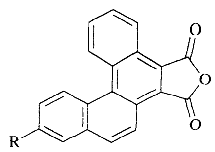
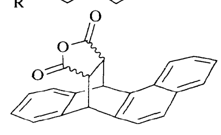
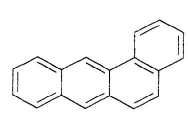
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140° ⇌	 + MA Substituent / (%)[b]: none 99; 9-Me 99; 9,10-Me_2 98; 9-Ph 75; 9,10-Ph_2 16; Benz[*a*] 84; diBenz[*a,h*] 30	1218
	140° ⇌	 (22) + MA	1218
	152° ⇌ $K_{eq} = 1.15 \times 10^{-2}$ M	 + MA	471
	140° ⇌	 (—) + MA	1219
	reflux $PhNO_2$	 (—) + MA	207
	rt - 100° ArH, $AlCl_3$	 (—) + MA ArH = benzene or *m*-xylene	207
	140° ⇌ $K_{eq} = 0.083$ M	 (—) + MA	472
	140° ⇌ $K_{eq} = 0.217$ <u>M</u>	 (—) + MA	472
	1. NaOH, EtOH, 78°, 0.5 h 2. H_3O^+	 (—) + 	225
	250°, S_8	 (25) + MA	1215
	290°, S_8	 R / (%): H 100; OMe 69 + MA	1215
	400 - 430°, soda lime	 (85)	1217

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

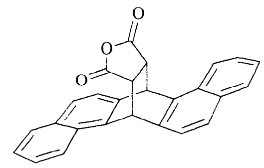
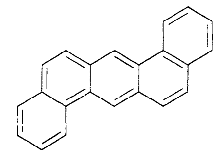
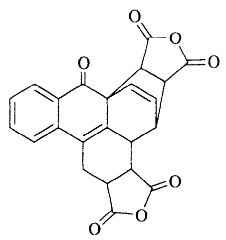
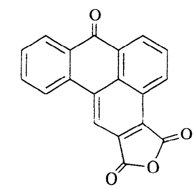
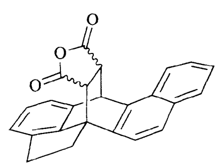
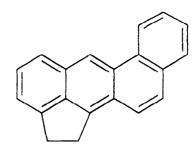
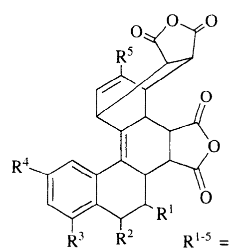
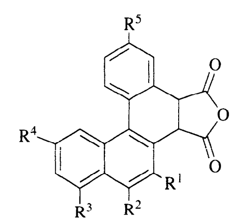
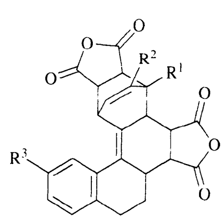
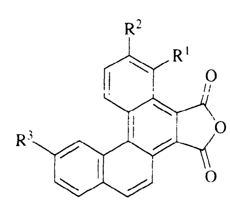
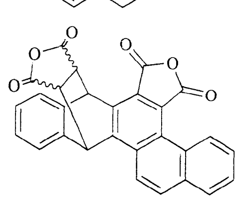
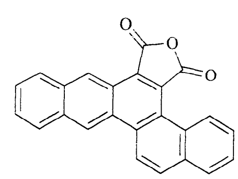
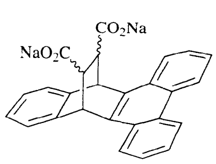
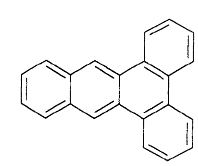
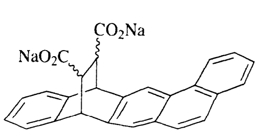
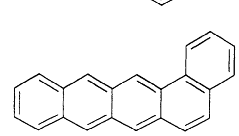
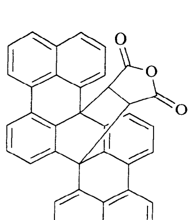
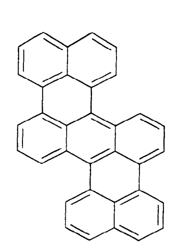
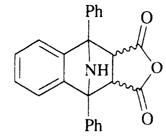
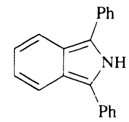
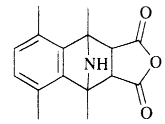
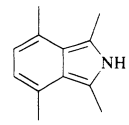
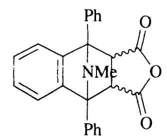
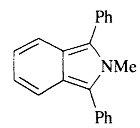
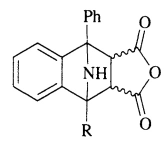
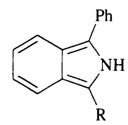
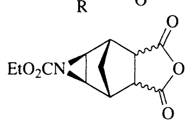
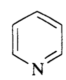
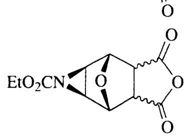
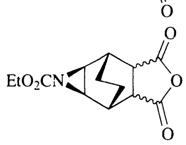
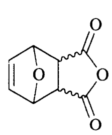
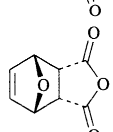
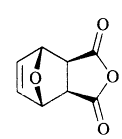
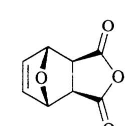
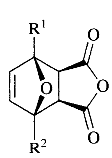
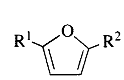
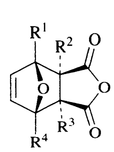
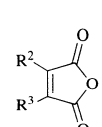
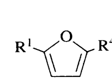
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	480°, soda lime	 (86)	1217
	$PhNO_2$, reflux (oxid.)	 (—) + MA	1220
	138° ⇄	 (—) + MA	1221
 R^{1-5} = mono-Me, all variants	heat (oxid.)	 (100) + MA	1222
	290°, S_8	 R[1] R[2] R[3] (%) H H OMe 80 H Me H 89 Me H H 87 H Ph H 0 H Cl H 77 + MA	1223
	300°	 (—) + MA	1224
	CO_2 stream, 320°	 (—) + MA	1225
	CO_2 stream, 320°	 (—) + MA	1225
	200°	 (—) + MA	1226

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	solvent, rt ⇄	 (—) + MA	1227
	rt, $CDCl_3$ ⇄	 (—) + MA	1228
	ca. 100° ⇄ rt	 (—) + MA	1229
 R = $CH_2CH_2CONEt_2$	solvent, rt ⇄	 (—) + MA	1230
	FVP, 725°	 (46) + MA (46) + EtOH + CO	1231
	FVP, 725°	MA + furan ("low")	1231
	FVP, 725°	MA + C_6H_6 + EtOH ("low")	1231
	rt ⇄	MA + furan	478, 473
	*ca.* rt ⇄	 (—)	138
mp 165° isomer	heat	mp 143° isomer	139
	acetone soltn., 5 min	MA + furan	140
	CH_3CN solvent, 40° $k = 4.37 \times 10^{-2}\ s^{-1}$ ⇄ $k = 7.29 \times 10^{-3}\ \underline{M}^{-1}s^{-1}$	MA + furan $\underset{k = 4.40 \times 10^{-6}\ s^{-1}}{\overset{k = 1.60 \times 10^{-5}\ \underline{M}^{-1}s^{-1}}{\rightleftarrows}}$  (—)	141
	33 - 59°; k (49.5°) s^{-1}	 (—) + MA	143

R^1	R^2	10^5 k	$\Delta H^{\#}$	$\Delta S^{\#}$
H	H	8.81	25.0	0.2
H	Me	6.92	20.8	-8.6
Me	Me	16.4	20.3	-2.2

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	*ca.* 50°	 (—) +  (—)	142

R^1	R^2	R^3	R^4	k(rel)
H	H	H	Me	1
H	D	D	Me	0.867
D	H	H	Me	0.932
H	D	H	Me	—
H	H	D	Me	—
H	H	H	CD_3	0.971

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

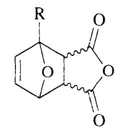
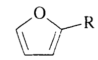
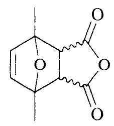
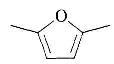
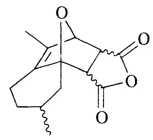
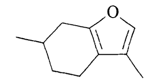
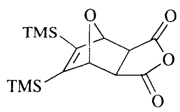
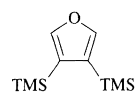
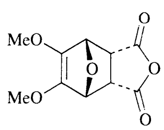
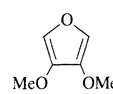
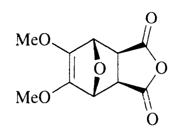
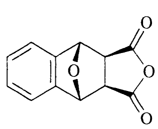
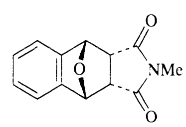
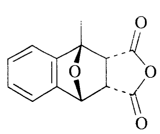
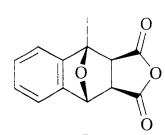
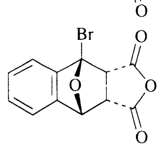
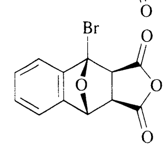
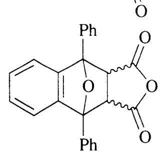
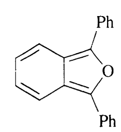
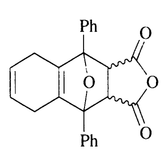
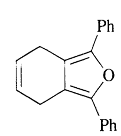
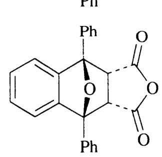
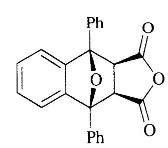
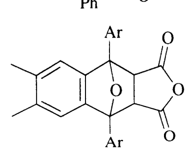
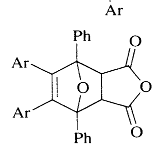
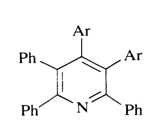
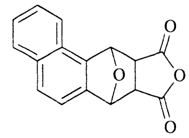
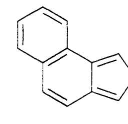
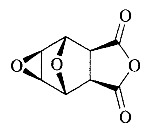
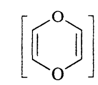
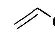
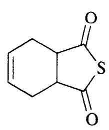
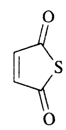
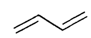
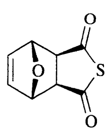
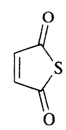
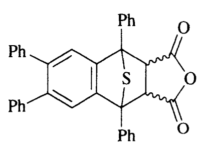
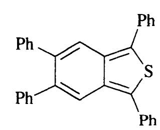
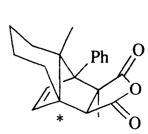
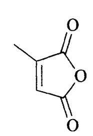
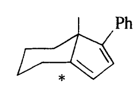
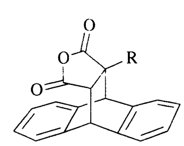
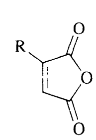
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = CH_2CH_2Ar, Ar = Ph or *m*-anisyl	> 70°, solvent ⇌ cool	 (—) + MA	1232
	rt ⇌	 (—) + MA	473
	heat ⇌	 (—) + MA	1233
	rt ⇌	 (—) + MA	298
	rt ⇌	 + MA ⇌ 	474
 + NMM	132°	 + MA	267
	80°, 24 h	 (—)	1072
	125°	 (—)	1234
	rt, solution ⇌	 (—) + MA	475
	rt, solution ⇌	 (—) + MA	1235
	heat	 (—)	476
	benzene, 80°	isomer; presumably *exo*	1236
 + PhCN	heat	 (—) + MA	1237

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	131° ⇌	 (—) + MA	1073
	FVP, 725°	 (15) ⟶ CO +  (20) + MA (40)	1231
	430°	 (45) + 	1238, 1239, 1240
	105°, 15 Torr	 (84) + furan	1241
	245°	 (—) + MA	1242
 (94)	rt, 1 atm (slow) ⇌ rt, 6.5 kbar, 10 d	 (—) + 	1066
	142° ⇌	 + $C_{14}H_{10}$	477

R	10^2 K_{eq}(M)	10^7 k_{rDA}(s^{-1})
H	0.0014	3.6
Me	0.44	13.3
Et	1.0	17.8
n-Pr	1.6	23.3
i-Pr	4.5	9.7
n-Bu	1.5	23.3
i-Bu	8.1	102
c-C_5H_9	2.4	1.1
c-$C_6H_{11}CH_2$	7.9	129
c-$C_6H_{11}(CH_2)_2$	1.8	32.8
Ph	0.18	ND
Br	0.0029	2.1

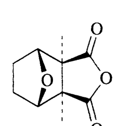
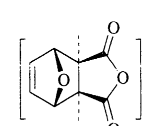
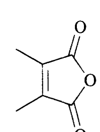
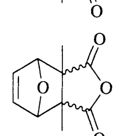
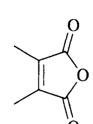
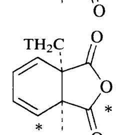
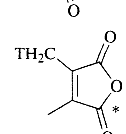
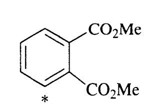
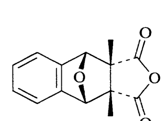
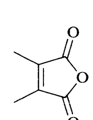
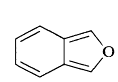
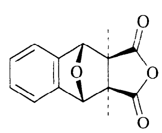
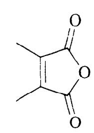
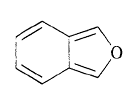
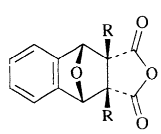
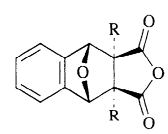
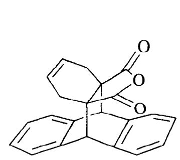
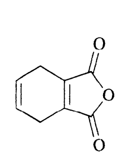
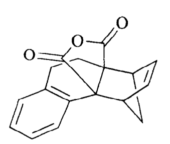
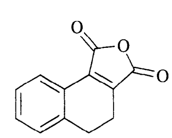
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 cantharidin	Pd, 280°	 ⟶  (—) + furan	478
	rt ⇌	 + furan	473
 + DMAD * = ^{14}C	180°, 17 h	 (97) +  (97)	1243
	112°	 +  (—)	1244

TABLE XI-F. MALEIC ANHYDRIDE (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	200°	 (—) +  (—)	1244
	132° ⇄	 (—) R / ΔG° / k_{exo} H / −2.4 / **$5.9 \times 10^{-6}s^{-1}$** Me / −1.9 / $150 \times 10^{-6}s^{-1}$ Cl / — / $190 \times 10^{-6}s^{-1}$ $(CH_2)_4$ / — / $87 \times 10^{-6}s^{-1}$	267
	vac. distill	 (—) + $C_{14}H_{10}$	1245
	melt, 158°	 (—) + CP	1246

[a] The starting material was defined as *endo* in this ref. and in the sub-table, although it is *exo* by IUPAC rules.

[b] This column shows the percent adduct at equilibrium.

[c] In MeCN, conversion to products is almost 100%.

TABLE XII. TRI- & TETRA-EWG ALKENES

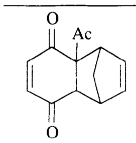
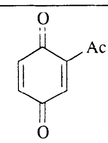
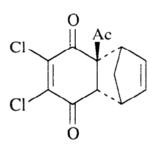
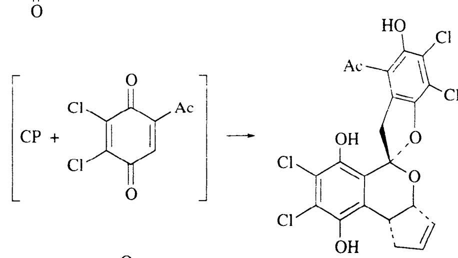
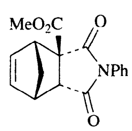
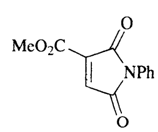
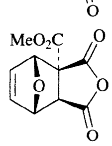
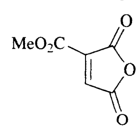
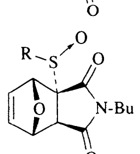
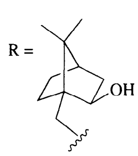
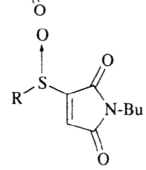
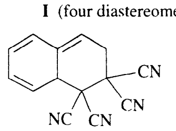
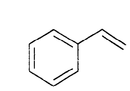
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	120°	 (—) + CP	1247
	80°, 6 h	 (100)	1248
	FVP, 650°	 (19) + CP	1249
	—	 (—) + furan	1250
 R =  **I** (four diastereomers)	—	furan +  (—) $\xrightarrow{ZnCl_2,\ 0°}$ **I** (two diastereomers)	1034
	⇌	TCNE +  (—)	1251, 1252

TABLE XII. TRI- & TETRA-EWG ALKENES (*Continued*)

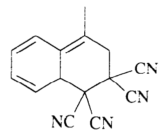
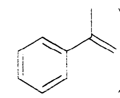
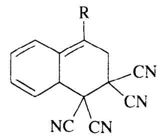
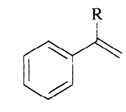
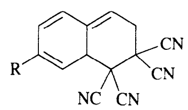
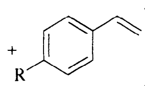
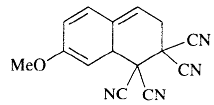
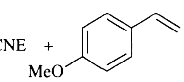
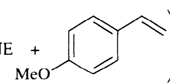
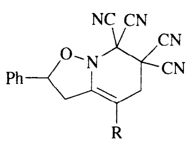
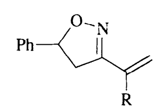
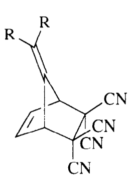
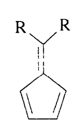
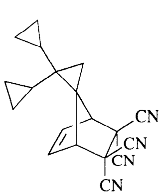
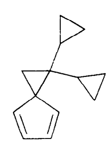
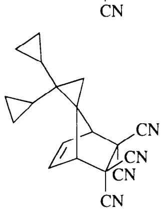
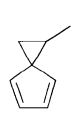
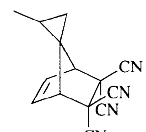
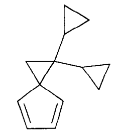
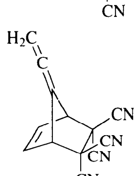
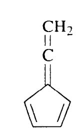
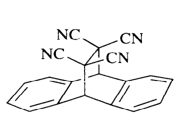
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	solvent ⇌ pressure	(TCNE + ) ⇌ educts (—) charge transfer complex	1253, 1254
	25° ⇌	TCNE +  (—) R = H, Me, or Ph	1255
	25°	(TCNE + ) charge transfer complex R / 10^4 k (s^{-1}): H 2.50; Me 14.5; Cl 3.72; Br 2.59	1256
	25° k = 0.123 x 10^{-4} s^{-1}	(TCNE + ) charge transfer complex	479
	pressure ⇌	(TCNE + ) charge transfer complex	1257
	rt - 60°	TCNE +  R / Temp / Time: H 60° 1 h ($t_{1/2}$); Ph rt 3 h	1258
	rt, $CHCl_3$ ⇌	TCNE +  (—) R / K_{eq} (M): p-$MeOC_6H_4$ 0.003; Ph 0.091; p-BrC_6H_4 0.303; p-ClC_6H_4 0.385; p-$O_2NC_6H_4$ 10.0; Me 0.031; Me, Et 0.014; $(CH_2)_5$ 0.008	480
	heat ⇌	TCNE +  (—)	1259
 + 	50°	 (—)  (—)	1260
	90 - 115°	TCNE +  (75)	1261
	40 - 60°	TCNE + $C_{14}H_{10}$ Solvent / ΔH# / ΔS#: MeOH 24.9 −2; EtOH 27.1 6; dioxane 27.5 7	481

TABLE XII. TRI- & TETRA-EWG ALKENES (*Continued*)

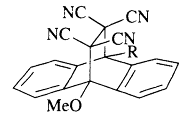
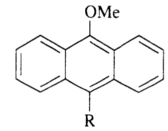
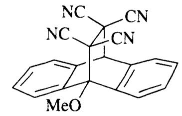
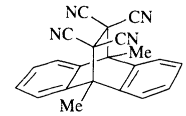
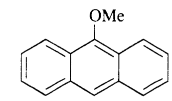
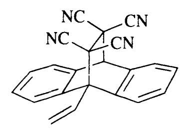
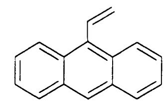
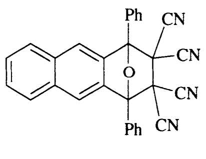
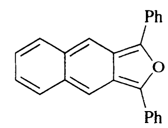
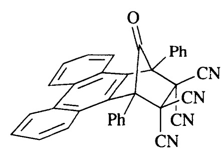
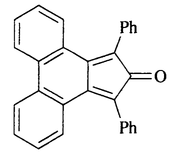
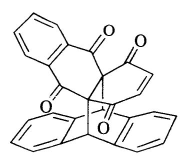
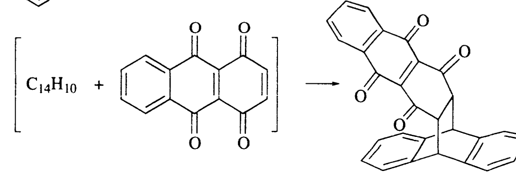
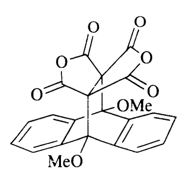
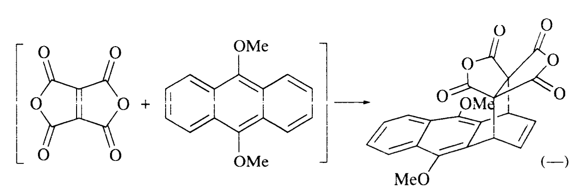
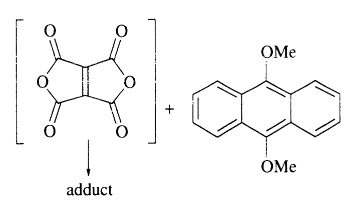
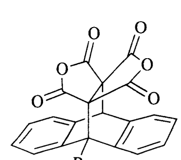
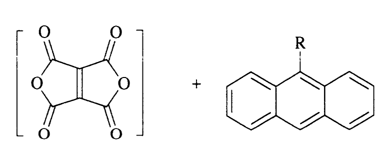
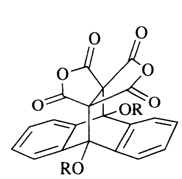
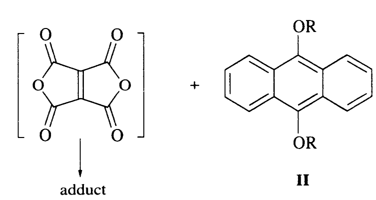
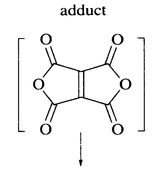
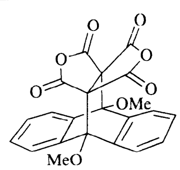
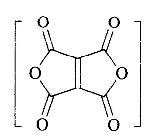
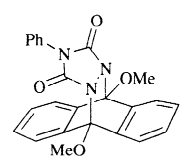
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = H or OMe	—[a]	 (—) + TCNE	1262
 + 9,10-dimethylanthracene	rt	 (97) +  (—)	269
	25° ⇌ $K_{eq} = 7 \times 10^{-5}$	 (—) + TCNE	1263
	80° ⇌ cool	 (—) + TCNE	1158
	65°	 (—) + TCNE	904
	100°	 (—) + enol tautomer	482
	10^{-3} M, dioxane	 (—)	271
	diene + solvent	 Diene — Adduct (%) CP — 81 2,3-diMe-C_4H_6 — 91 diMe-fulvene — 56 diPh-fulvene — 60 chloroprene — 60 1,4-diPh-C_4H_6 — 81	271
 R = Cl, OMe, or Ph	solvent	 (—)	271
 + diene R = Me or Et diene = CP, diMe-fulvene, or norbornadiene [2+2+2]	dioxane, 101°	 (—)	270
I + CP	dioxane, 40°	 + II (—) R — k (s^{-1}) Me — 1.5×10^{-4} Et — 1.7×10^{-3}	269, 273

TABLE XII. TRI- & TETRA-EWG ALKENES *(Continued)*

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 + PTAD	K_{eq} = *ca.* 0.06 ⇄	 +  (—)	273

[a] The starting material "suffers intense retro-degradation."

TABLE XIII-A. NITROGEN-SUBSTITUTED ALKENES

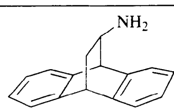
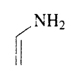
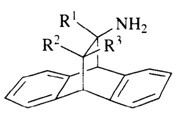
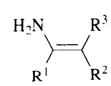
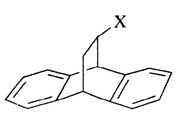
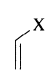
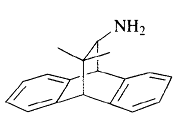
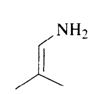
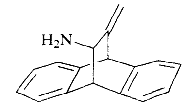
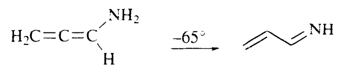
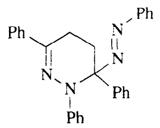
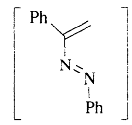
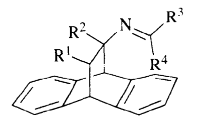
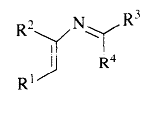
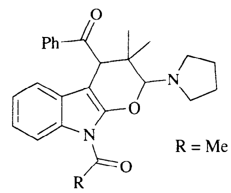
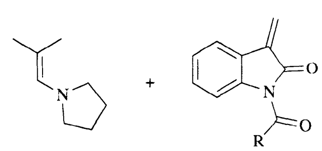
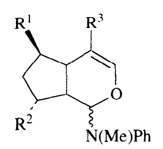
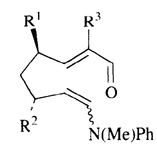
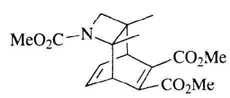
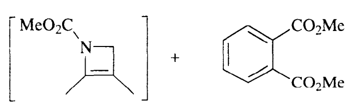
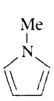
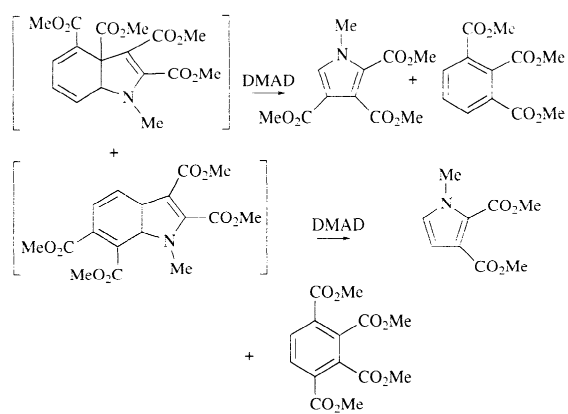
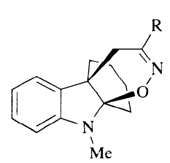
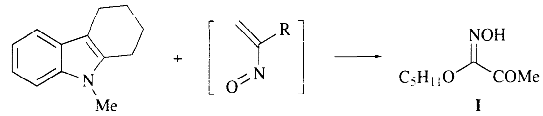
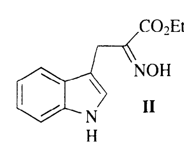
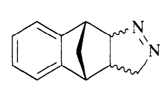
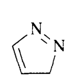
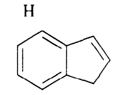
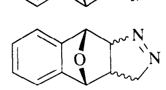
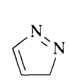
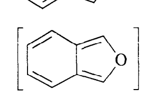
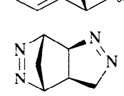
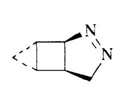
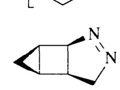
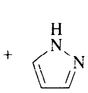
Starting Material				Conditions	Product(s) and Yield(s) (%)			Refs.
				FVP, 600°	 (—) + $C_{14}H_{10}$			1264
	R^1	R^2	R^3	FVP, 600°	 (*ca.* 70) + $C_{14}H_{10}$			1265
	H	H	H					
	H	H	H (ND_2)					
	H	Me	H					
	H	H	Me					
	Me	H	H					
	Me	H	Me					
	Me	Me	H					
				250°	 (—)	X	k_{rel}	175, 176
					+ $C_{14}H_{10}$	OAc	0.30	
						H	1*	
						OH	1.3	
						OMe	2.2	
						OTMS	2.3	
						NHAc	14	
						TMS	16	
						NO_2	17	
						NH_2	83	
						NH_3+	1,680	
						NMe_2	2,480	
						*k = $1.21 \times 10^{-5} s^{-1}$		
				FVP, 600°	 (25) + $C_{14}H_{10}$			1266

TABLE XIII-A. NITROGEN-SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 790°	 (20) + $C_{14}H_{10}$	485, 484
	rt, HOAc	 (—)	1267
 R_1, R_2, R_3 = H or Me; R_4 = Me, Et, or Ph (11 examples)	FVP, 450°	 (75 - 80) + $C_{14}H_{10}$	1268
 R = Me or Ph	35°, $CDCl_3$	 (—)	1269
 R[1] R[2] R[3]: Me H H; H Me H; H Me Me	rt, or silica gel ⇌		1270
	200 - 325°	 (—)	1031
 + DMAD	warm		1271
	140°, solvent	 or 	1272
	190 - 200°, 20 Torr	 (60) +  (67)	1273
	180°, Cu	 (—) + 	1274
	120°	 (—) +  (—) +  (—) ratio 2 : 1 : 1	1275

R	Solvent	(%)
COMe	pentanol	67 (I)
CO_2Et	indole	— (II)

TABLE XIII-A. NITROGEN-SUBSTITUTED ALKENES (*Continued*)

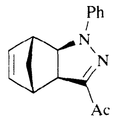
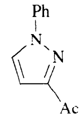
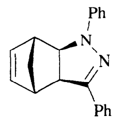
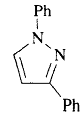
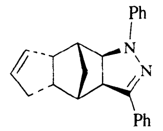
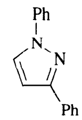
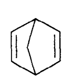
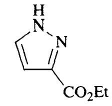
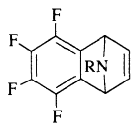
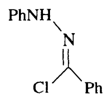
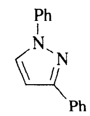
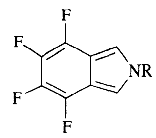
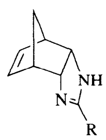
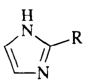
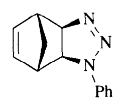
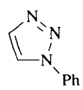
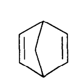
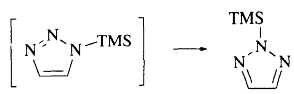
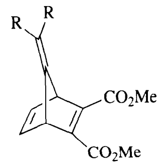
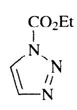
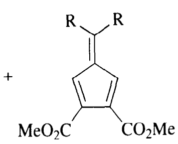
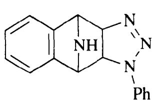
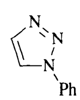
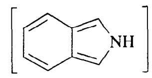
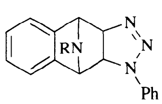
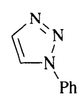
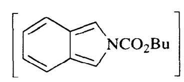
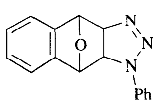
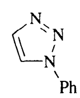
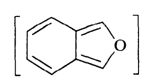
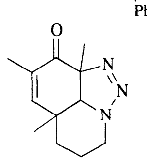
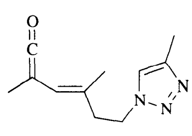
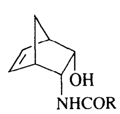
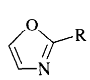
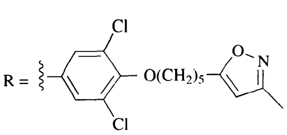
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	140°	 (—) + CP	1276
	135°	 (98) + CP (77)	1277
	Pt/C, 300°; or S, 225°	 (46)	1277
 + N_2CHCO_2Et	rt; $Fe(CO)_5$ or $Co_2(CO)_8$ catalyst	 (95) + CP (95)	1278
 + 	Et_3N, rt	 +  R (%): H 77; Me 90	1279
	190 ± 5°	 R (%): H 40; Me 79; Et 60; Bu 73; Ph 54; OEt 70 + CP	1280
	120°, 2 h	 (79) + CP	402
 + $TMSN_3$	130°	 (80) + CP	486
 + N_3CO_2Et	—	 I +  II; R, I (%), II (%): Me 20 —; Ph 45 90	1281
	70°	 +  (—)	1282
 R = CO_2Bu	120°	 +  (—)	1283
	170°	 (63) +  (—)	802
	UV	 (—)	1284
	183°, 4.5 h	 (85) + CP R = 	1285

TABLE XIII-A. NITROGEN-SUBSTITUTED ALKENES (*Continued*)

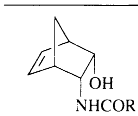
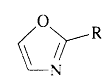
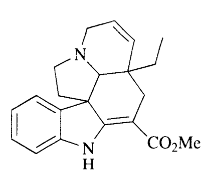
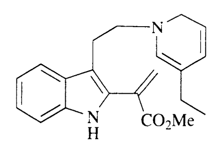
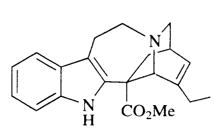
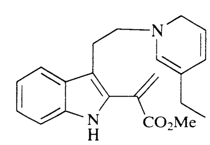
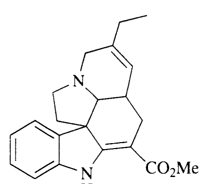
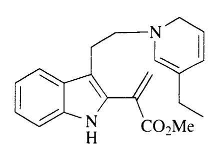
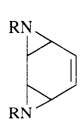
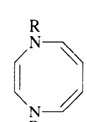
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	190°	 R (%): H 49; Me 63; Et 61; Bu 88; Ph 84 + CP	1280
	205°	 (—)	1286
	140°	 (—)	1286
	175°	 (—)	1286
 R = mesityl	54°	 (100)	1287

TABLE XIII-B. *O*-SUBSTITUTED ALKENES

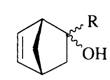
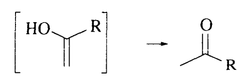
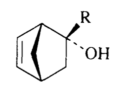
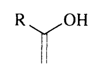
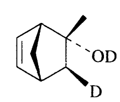
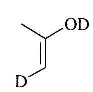
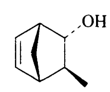
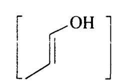
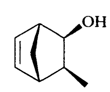
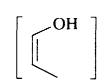
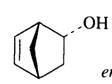
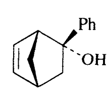
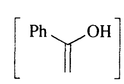
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = H, Me, vinyl, allyl, *n*-Bu, cyclopropyl	FVP, 500°	 (100) + CP	1288
 R = Me, $^{13}CH_3$, or CD_3	FVP, 800°	 (—) + CP	487
	FVP, 800°	 (—) + CP	487
	FVP, 800°	 (—) + CP	1289
	FVP, 800°	 (—) + CP	1289
 *endo*	2 eq PhMgBr, ether, reflux 24 h	$PhCHOHCH_3$ (40-50) + CP (5)	230, 227
	$MgBr_2$ or NaH, ether, reflux 24 h	CH_3CHO (—) + CP	230
	$MgBr_2$, PhCHO, ether, reflux, 24 h, trace NaOH	PhCH=CHCHO (—) + CP	230
	FVP, 770 - 800°	 (—) + CP	1290

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

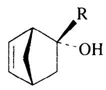
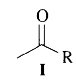
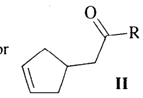
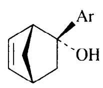
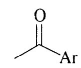
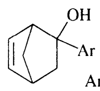
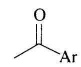
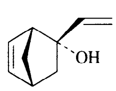
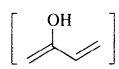
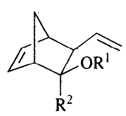
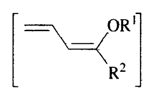
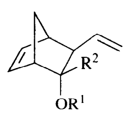
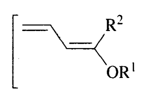
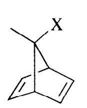
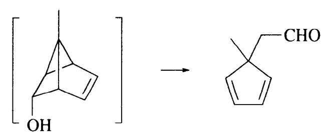
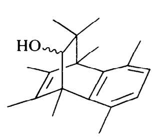
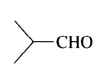
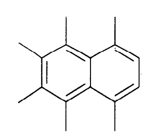
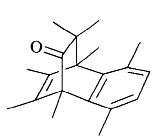
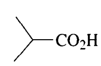
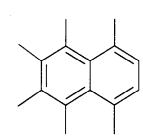
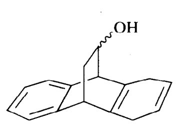
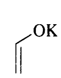
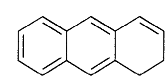
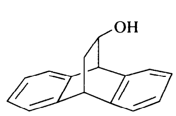
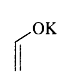
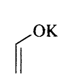
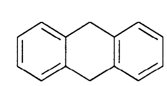
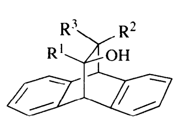
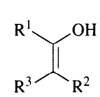
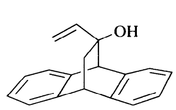
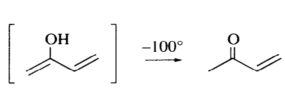
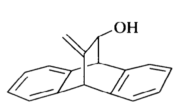
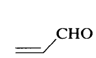
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 90% *endo*	KH, HMPA, 30°	 I + CP or  II R / I (%) / II (%): various alkyl 0, 12 - 92; Ph 62, 8; Bn 6, 85	231
 Ar = *p*-ClC$_6$H$_4$	KH, 18-[c]-6, THF, rt	 (100) + CP	232
 Ar = *o*, *m*, & *p*-tolyl; *o*,*m*, & *p*-anisyl; 2- & 3-thiophenyl; 2- and 3-pyridyl; *p*-vinylphenyl	KH, 18-[c]-6	 (≥70) + CP	233
	FVP, 800°	 (—) + CP	1291
 R^1 R^2: H H; H D; D H	FVP, 750°	 (—) + CP	1292
 R^1 R^2: H H; H D; D H	FVP, 750°	 (—) + CP	1292
 X = *p*-nitrobenzoate	NaOAc, 75° aq. acetone	 (59)	251
	NaH, DMSO, 75°, 17 h	 (—) +  (95)	238
	NaH, DMSO, 75°, 4.5 h	 (—) +  (87)	238
	KH, THF, rt, 18 h	 +  (69)	227
	KH, THF/HMPA, rt, 66 h	 + C$_{14}$H$_{10}$ (60)	227
	KH, dioxane, 101°, 3 h	 +  (79)	227
 R's = H or Me (8 examples)	FVP, 550°	 (—) + C$_{14}$H$_{10}$	1293
	FVP	 (90) + C$_{14}$H$_{10}$	485
	FVP	[H$_2$C=C=C(OH)H] $\xrightarrow{-50°}$  (45) + C$_{14}$H$_{10}$	485, 484

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

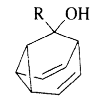
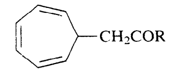
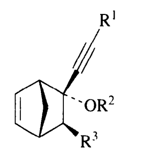
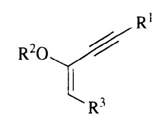
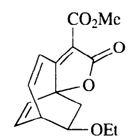
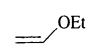
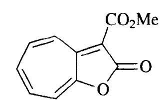
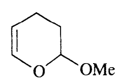
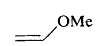
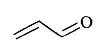
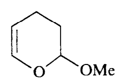
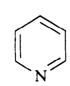
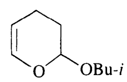
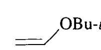
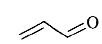
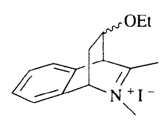
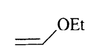
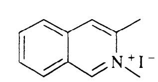
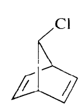
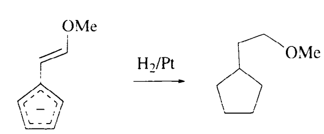
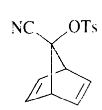
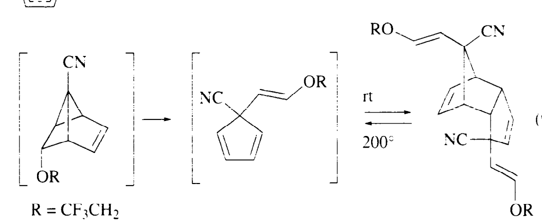
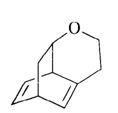
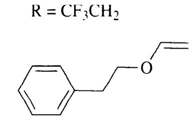
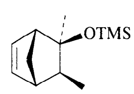
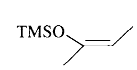
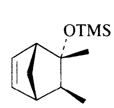
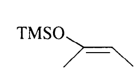
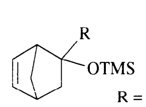
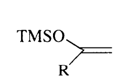
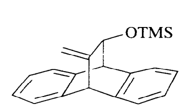
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	KH, 18-[c]-6, THF, 30 - 60°	 I R / I (%) / E_a / logA H or Me / NR / — / — vinyl / 60 / — / — p-BrC_6H_4 / 86 / 15.8 / 8.3 p-ClC_6H_4 / 98 / 16.2 / 8.4 Ph / 90 / 17.9 / 9.7 p-MeC_6H_4 / 91 / — / — p-$MeOC_6H_4$ / 81 / 22.5 / 12.9	232
 R^1 R^2 R^3 H H H D H H H H D H D H	vapor pyrolysis	 (—) + CP	1294
	150°, 10 kbar	 (—) +  (—)	1295
	296 - 353° E_a = 48.5	 (100) +  (100)	1296
 + NH_3	400°, SiO_2/Al_2O_3	 (—)	1297
	400°	 (94) +  (—)	1298
	MeCN, 81°	 +  (100)	1299
	NaOMe, MeOH	 (22)	250
	CF_3CH_2OH, 25°	 (90) R = CF_3CH_2	1300
	heat, or UV	 (—)	1301
	FVP, 500°	 (100) + CP	732
	FVP, 500°	 (100) + CP	732
 R = vinyl, allyl, n-Bu, cyclopropyl	FVP, 500°	 (100) + CP	1288
	FVP	$H_2C{=}C{=}C(OTMS)H$ (60) + $C_{14}H_{10}$	485

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

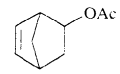
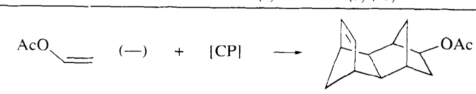
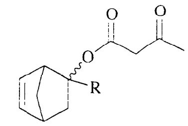
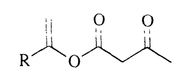
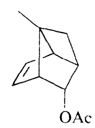
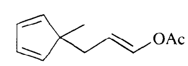
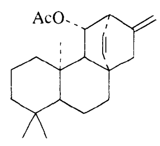
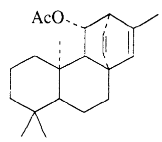
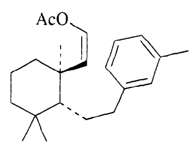
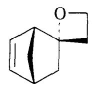
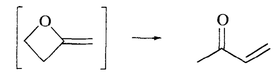
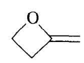
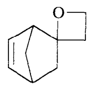
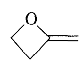
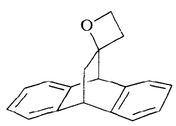
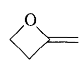
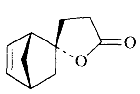
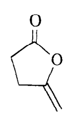
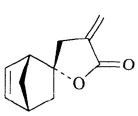
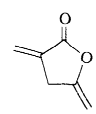
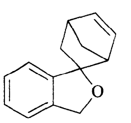
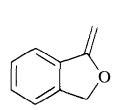
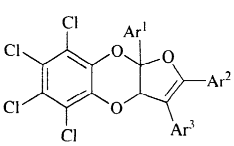
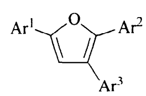
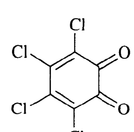
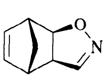
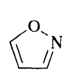
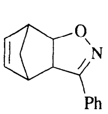
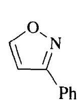
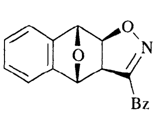
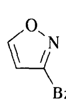
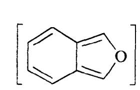
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	170 - 250°	 (100)	1302, 491
	FVP, 575 - 625°	 R (%): H 61, Me 48 + CP	1303
	heat (GLC)	 (—)	1304
	TsOH, pyridine, 112°	 (22) +  (37)	688
	400°, gas phase	 (—) + CP	490
	FVP, 600°	 (70) + CP	490
	FVP, 550°	 (90) + CP	1305
	330°	 (10) + $C_{14}H_{10}$	1306, 1307
	heat	 (100) + CP	710
	FVP, 550°	 (83) + CP	1308
	FVP, 500 - 550°	 (—) + CP	1305
 Ar = various	UV	 (—) + 	1309
	140 - 160°	 (90) + CP	1310
	170°	 (—) + CP	1311, 1312
	160°, 5 h	 (40) + 	802

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

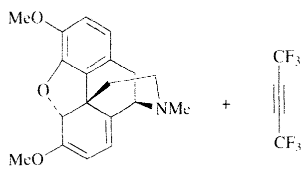
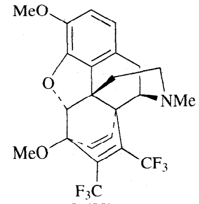
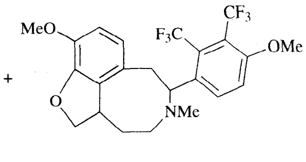
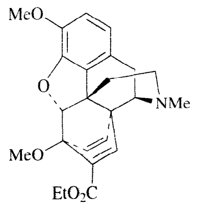
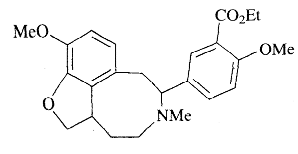
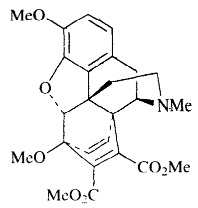
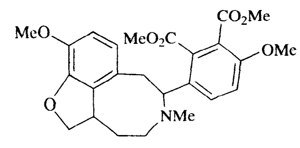
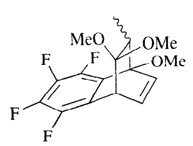
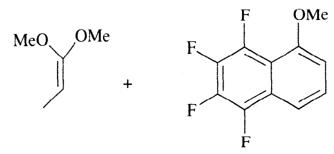
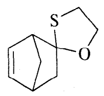
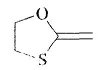
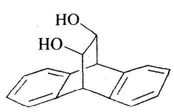
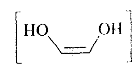
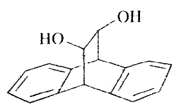
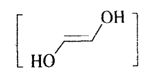
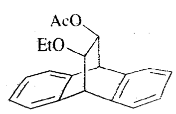
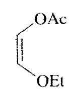
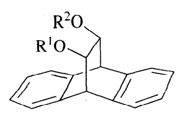
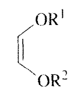
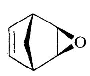
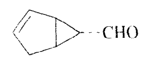
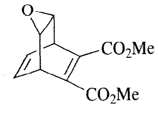
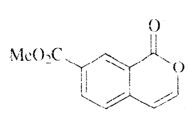
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
 thebaine	50°, 18 h	 **I (38)** +  **II** (39)	492
I	80°, 0.5 h	**II**	
	50°	 ("low")	1313
	141°	 (—) + DMAD + thebaine	1313
	300°	 (87)	1314
	FVP, 500°	 (65) + CP	1305
	FVP, 600°	 (—) + $C_{14}H_{10}$	1315
	FVP, 600°	 (—) + $C_{14}H_{10}$	1315
	300°	 (87) + $C_{14}H_{10}$	1316
	300°	 + $C_{14}H_{10}$ R^1 / R^2 / (%) TMS / TMS / 97 Ac / Ac / 53 Et / TMS / 89 Et / $SiMe_2Ph$ / 36 Et / TBDMS / 79	1317
rDA attempts to prepare 			
	rt		489
	heat	"no definitive products"	1318
	FVP, 700°	 (—)	1319

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

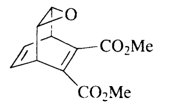
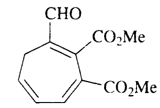
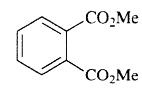
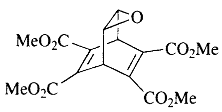
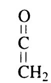
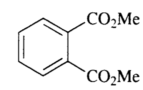
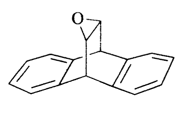
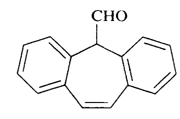
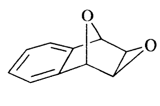
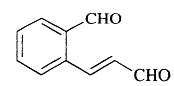
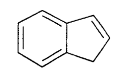
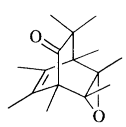
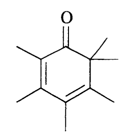
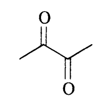
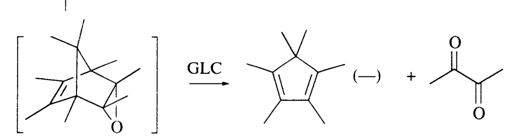
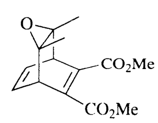
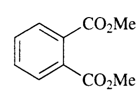
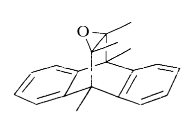
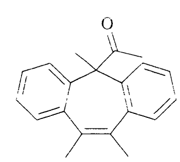
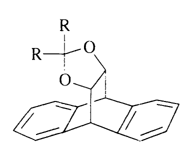
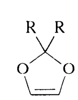
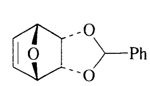
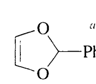
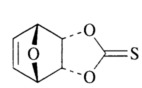
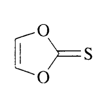
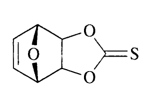
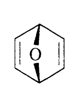
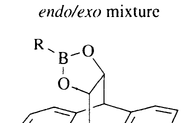
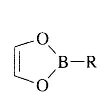
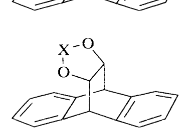
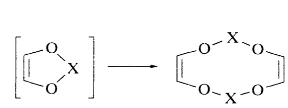
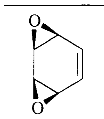
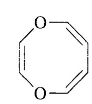
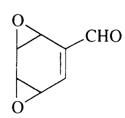
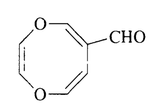
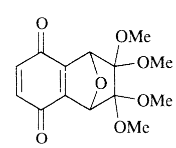
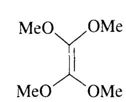
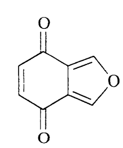
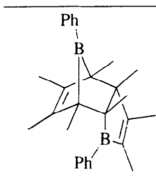
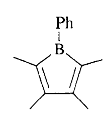
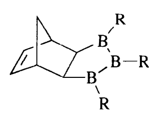
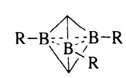
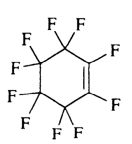
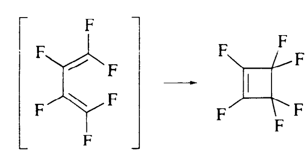
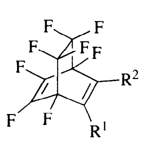
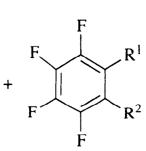
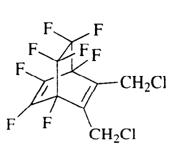
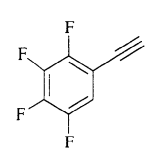
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	"flash", 300°	 (62)	1320, 1321
	700°	 (5) +  (3)	1321, 1320
	600°	 (10) +  (10 - 20)	1320
	400°	 (75)	1320
	FVP, 600°	 (50) +  (50)	1322
	GLC, 190°	 (20) +  (10)	1323
	UV	 (—) + (—)	1323
	500°	 (5) +  (2 - 5)	1320
	trace H^+	 (—)	1324
	pyridine, heat	no reaction	
	flame, N_2	 R (%): H 35; Me 49 + $C_{14}H_{10}$	1325
	170°	 [a] (15) + furan	1326
	160°	 (*ca.* 100) + furan	1326
 + $P(OEt)_3$ *endo/exo* mixture	heat	 **I** + furan **II**; Temp / **I** (%) / **II** (%): 110° 60 20; 150° 1 : 4	488
	FVP, 550°	 (100) + $C_{14}H_{10}$ R = OMe, Ph, *o*-tolyl, 2,6-dimethylphenyl, cyclohexyl	1327, 1328
	FVP, 560°	 X (%): $SiMe_2$ 97; $SiEt_2$ 89; Si(Et)Me 90; Si(Me)Ph 41 + $C_{14}H_{10}$	1317

TABLE XIII-B. *O*-SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	≥ 50° ⇄	 (—)	1329
	acetone, 54°	 (94)	1330
	200°, 0.1 Torr	 (—) +  (—)	494

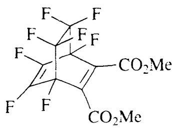
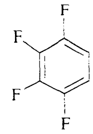
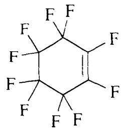
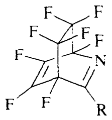
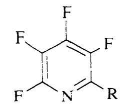
[a] This unstable product was trapped by in situ anthracene.

TABLE XIII-C. OTHER HETEROATOM-SUBSTITUTED ALKENES

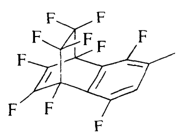
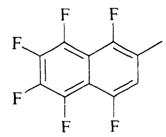
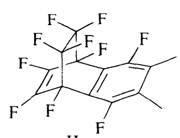
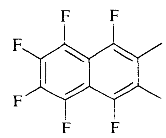
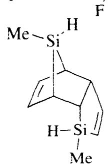
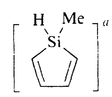
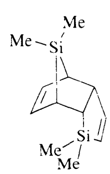
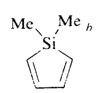
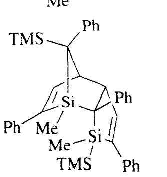
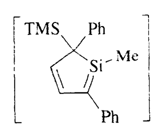
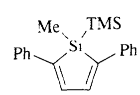
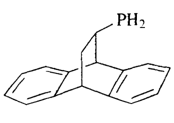
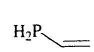
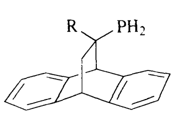
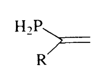
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	≥ 60° (⇄)		1331
 R = N(Pr-*i*)$_2$	vacuum sublimation	 (2) + CP 2,3,4-tris(diisopropylamino)-1,5-dicarba-*closo*-pentaborane	1332
	SF_6, IR laser E_a ≥ 66	C_2F_4 +  (—)	1333-1337
	550 - 630°	C_2F_4 + 	1338
	600°	C_2F_4 +  (—)	1338

R^1	R^2	(%)
H	Me	95
H	CF_3	94
H	CH_2Cl	—
H	Ph	71
Me	Me	99
CF_3	CF_3	97
Me	CF_3	95

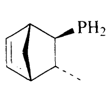
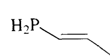
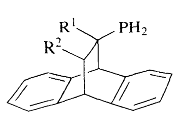
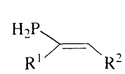
TABLE XIII-C. OTHER HETEROATOM-SUBSTITUTED ALKENES (Continued)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	550°	 (major) + C_2F_4	1338
 + RCN	heat	 I →  II + C_2F_4	1339

R	Temp	Time	I (%)	II (%)
CF_3	400°	16 h	0	40
Br	400°	15 h	0	40
Br	380°	12 h	9	18
C_6F_5	390°	64 h	0	4
$(CF_2)_3CN$	350°	16 h	4	1
$(CF_2)_3CN$	350°	64 h	0	10

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 540 - 630°	 (70) + C_2F_4	1340
	FVP, 600°	 (—) + C_2F_4	1340
	≥100°	 [a] (—)	1341
	FVP ⇌ −37°	 [b]	1342
	K_{eq} (150°) = 1 ⇌	 I (—) +  II → II	1343
	FVP, 650°	 [c] (70) + $C_{14}H_{10}$	496
	FVP	 + $C_{14}H_{10}$	1344

R	Temp	(%)
H	550°	—
Me	700°	—

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 450°	 (25) + CP	1345
	FVP, 450°	 + $C_{14}H_{10}$	1345

R^1	R^2	(%)
H	H	70
Me	H	55
H	Me	25

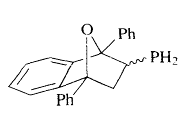
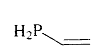
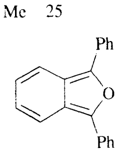
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 400°	 (—) +  (100)	496

TABLE XIII-C. OTHER HETEROATOM-SUBSTITUTED ALKENES (*Continued*)

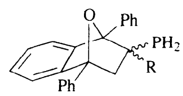
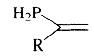
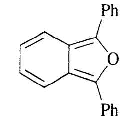
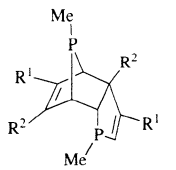
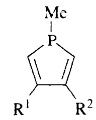
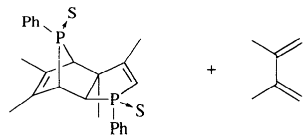
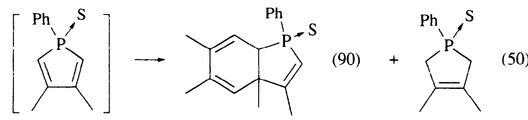
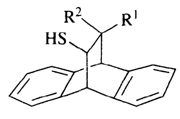
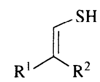
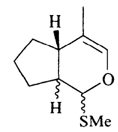
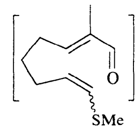
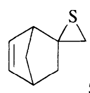
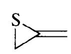
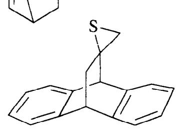
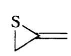
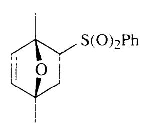
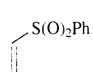
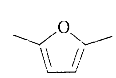
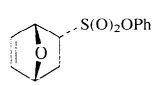
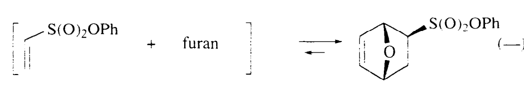
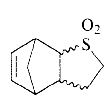
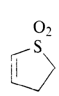
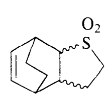
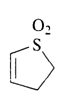
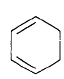
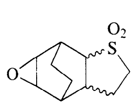
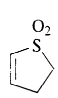
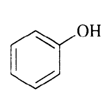
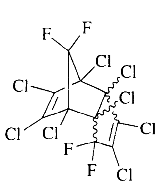
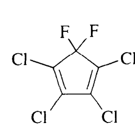
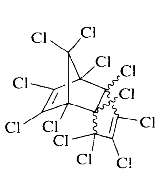
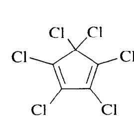
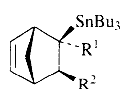
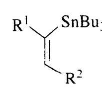
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 450°	 R (%): H —; Me 30 +  (—)	1345
	FVP, 400°	 R¹ R² (%): H H 97; Me H 91; Me Me 94	1346
	150°		1347
	FVP, 625°	 (—) R¹ R²: H H polymerizes at rt; H, Me stable in solution at rt; Me Me stable in solution at rt + $C_{14}H_{10}$ (100)	495
	−78°, $BF_3•Et_2O$ (⇌)	 (—)	1348
	FVP, 600 - 700°	 (—) + CP	1349
	520°	 (—) + $C_{14}H_{10}$	1349
	K = *ca* 1 (⇌)	 (—) +  (—)	1350
	70° (⇌)	 (—)	1350
	FVP, 750°	 (85) + CP (70)	1231
	FVP, 675°	 (21) +  (11)	1231
	FVP, 750°	 (—) +  (73)	1231
	480°	 (—)	1351
	340°	 (—)	1352

TABLE XIII-C. OTHER HETEROATOM-SUBSTITUTED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)					Refs.
	FVP, 400°		R^1	R^2	(%)		
			OCH_2OMe	H	98	+ CP	1353
			OBn	H	95		
			$O(CH_2)_2OMe$	H	95		
			OCH_2OMe	Me	85		
			OCH_2OMe	CH_2OBn	98		
			H	OCH_2OAc	75		
			H	$OCH_2O(CH_2)_2OMe$	70		

[a] This product was trapped in situ by MA or other dienophiles.

[b] This product was detected by NMR at –70°.

[c] This product decomposes at rt, $t_{1/2}$ = 8 d (CCl_4).

TABLE XIV. KETENES AND RELATED ALKENES

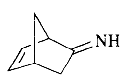
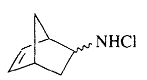
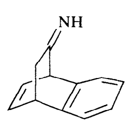
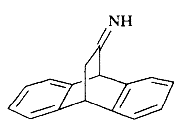
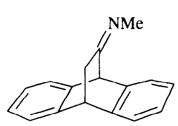
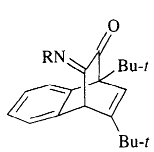
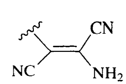
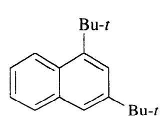
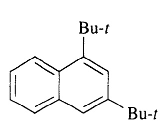
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	FVP, 850°	[$H_2C{=}C{=}NH$] (decomp. > −150°) + CP	498
	FVP	[$H_2C{=}C{=}NH$] + MeCN + CP + HCl	1354
	FVP, 800°	[$H_2C{=}C{=}NH$] (decomp. > −150°) + MeCN + $C_{10}H_8$	498, 1354
	FVP, 800°	[$H_2C{=}C{=}NH$] + MeCN + $C_{14}H_{10}$	498, 1354
	FVP, 650°	$H_2C{=}C{=}NMe$ (75) + CH_3CH_2CN (20) + $C_{14}H_{10}$	1266
 R = 	UV	 (63) + RNC + CO	407
R = Pr, hexyl, Ph, or OH	UV	 (—) + RNC ("good") + CO	408, 407

TABLE XIV. KETENES AND RELATED ALKENES (*Continued*)

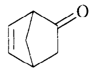
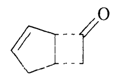
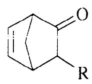
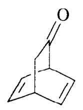
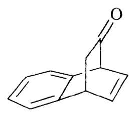
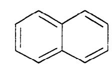
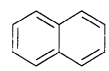
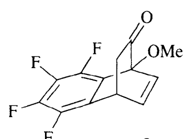
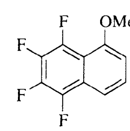
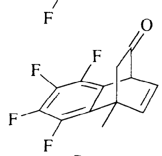
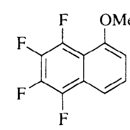
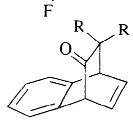
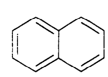
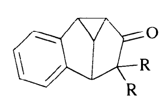
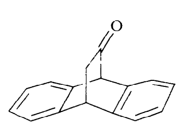
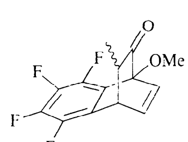
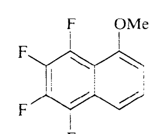
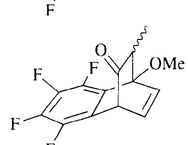
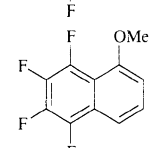
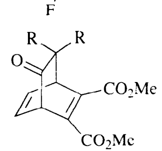
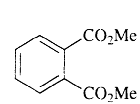
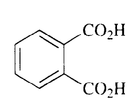
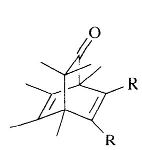
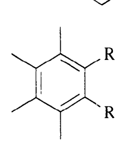
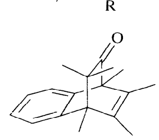
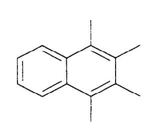
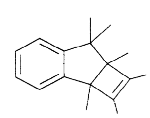
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV	$H_2C{=}C{=}O$ (100) + CP (100)	1355
	UV	 $\xrightarrow{UV}$ $H_2C{=}C{=}O$ (—) + CP	499
	FVP, 600°	H(R)C=C=O (100) + CP	1356
	180°	no reaction	497
	UV	$H_2C{=}C{=}O$ +  (77)	1357
	UV, acetone sensitized	 (23)	1357
	300°	$H_2C{=}C{=}O$ +  (79)	1314
	300°	$H_2C{=}C{=}O$ +  (94)	1314
 R = H or D	UV, acetone sensitized	 (20) +  (70)	1358
	UV	$H_2C{=}C{=}O$ (60) + $C_{14}H_{10}$ (44) + $(C_{14}H_{10})_2$ (19)	1359, 1360
	350°	C=C=O (H) +  (71)	1314
	300°	C=C=O (H) +  (98)	1314
 R, R: Me, Me; —$(CH_2)_5$—	500°	$R_2C{=}C{=}O$ (—) + 	237
	1. KOH, rt, 4 h 2. aq. acid	R_2CHCO_2H (—) + 	237
	UV, ether	C=C=O +  R (%): CO_2Et 80; Ph 83	1361
	UV, ether	C=C=O +  (71) +  (—)	1361

TABLE XIV. KETENES AND RELATED ALKENES (*Continued*)

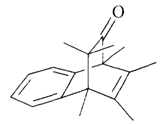
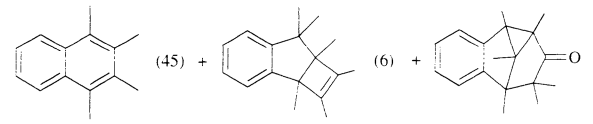
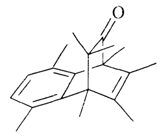
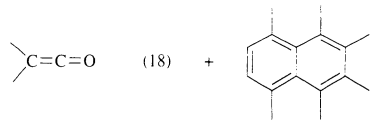
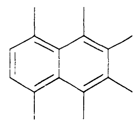
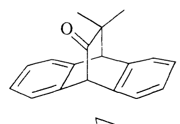
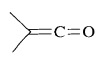
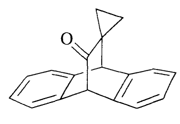
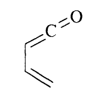
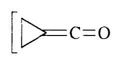
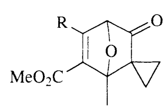
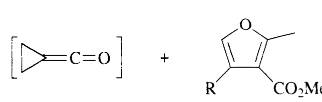
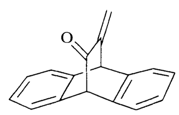
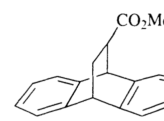
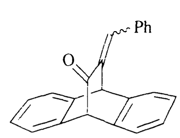
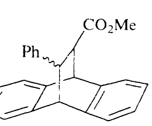
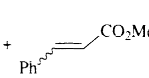
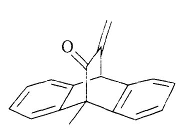
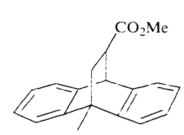
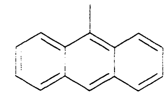
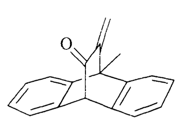
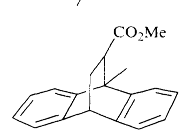
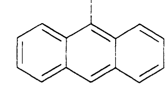
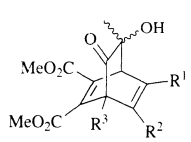
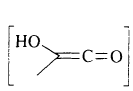
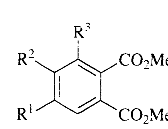
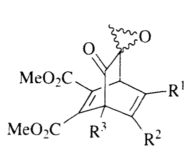
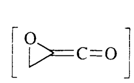
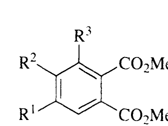
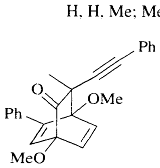
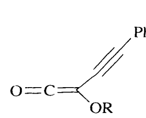
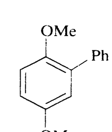
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, acetone sensitized	 (45) + (6) + (26)	1362
	450°	 (18) + (18)	238, 1363
	$NaCH_2S(O)CH_3$, 70°; or 1. $LiAlH_4$ 2. NaH, DMSO	 (96 - 100)	238, 1363
	FVP, 700°	 (70) + $C_{14}H_{10}$	1364
	FVP, 750°	 (35) + $C_{14}H_{10}$	1365
	UV	 (100) + $(C_{14}H_{10})_2$	1365
	UV, Pyrex	 R (%): H 50; CO_2Me 65	1366
	UV, MeOH	 (93) + $C_{14}H_{10}$ (≤ 1%)	501, 1367
	UV, MeOH	 (60) +  [a] (40) + $(C_{14}H_{10})_2$ (40)	501, 1367
	UV, MeOH	 (—) +  (2)	501
	UV, MeOH	 (32) +  (4)	501
 R^1, R^2, R^3 = H, H, Me or Me, H, Me	UV	 (—) + 	1368
 R^1, R^2, R^3 = Me, H, H; Me, Me, H; H, H, Me; Me, H, Me; or tBu, H, Me	UV	 (66) + 	1368
	138°	 R (%): H ≥34; TMS ≥55 + 	1369

TABLE XIV. KETENES AND RELATED ALKENES (*Continued*)

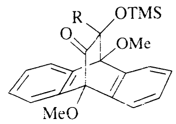
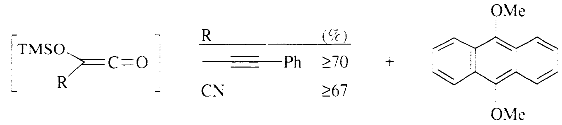
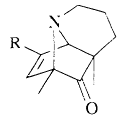
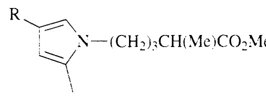
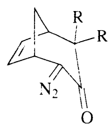
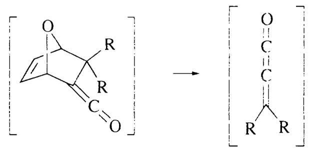
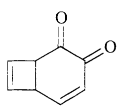
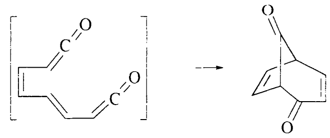
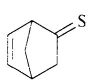
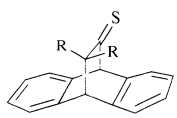
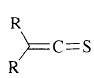
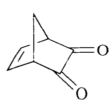
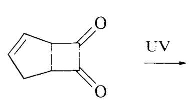
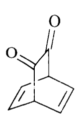
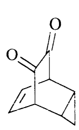
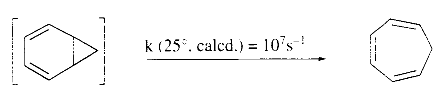
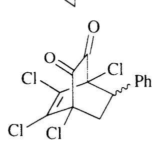
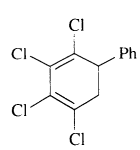
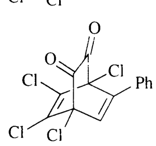
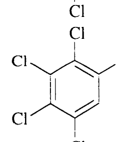
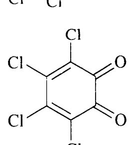
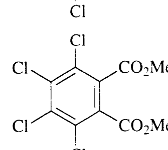
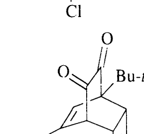
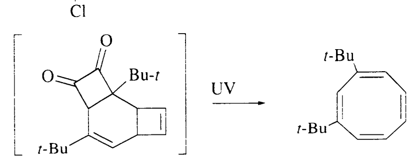
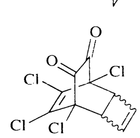
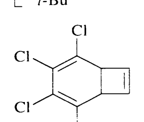
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	220°		1370
 R = Me or *t*-Bu	UV, MeOH	 (100)	1371
 R, R = H, H or Me, Me	FVP, 430°	 + furan (—)	1372
	150°, or GLC	 (11)	1373
	FVP, 700°	[H$_2$C=C=S] (≥ 51) + CP	509, 331
	FVP, 700°	 R (%): H —; Me ≥60 + C$_{14}$H$_{10}$	509
	UV, 404 nm	 CO + CP	506[b], 1374
	"thermally stable"		504
	calculations	thermal reaction is "spin forbidden"	1375
	ab initio	O=C=C=O unstable relative to 2 CO	502
	UV, −196°		1376
	UV	 (≥ 60) + CO	1359
	180°, or UV	 Cond (%): 180° 32; UV 97 + CO	1359, 1377, 1378
 + DMAD	heat	 (—) + CO	1379
	UV	 (84)	1380
 *endo/exo* mixture	UV	 (—) + CO	781

TABLE XIV. KETENES AND RELATED ALKENES (*Continued*)

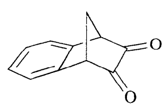
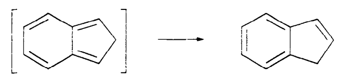
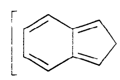
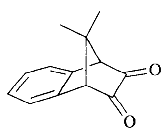
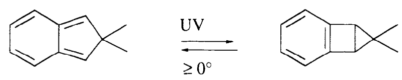
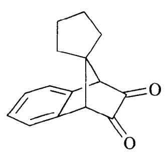
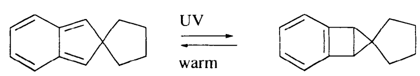
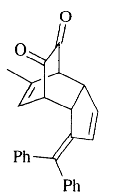
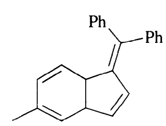
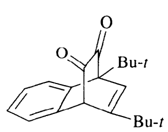
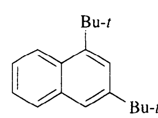
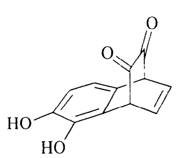
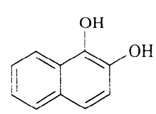
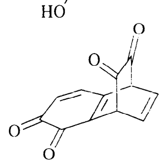
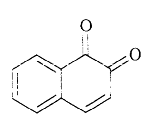
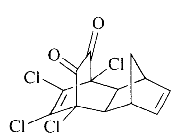
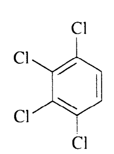
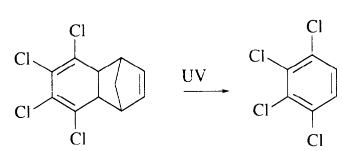
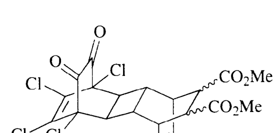
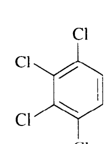
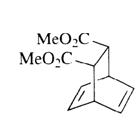
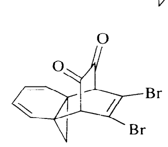
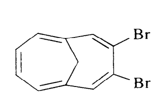
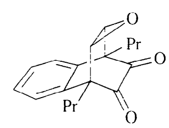
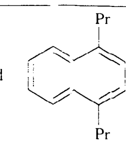
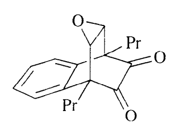
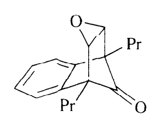
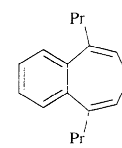
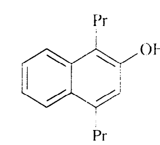
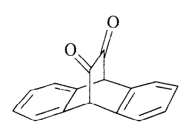
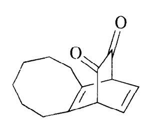
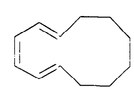
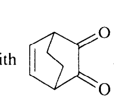
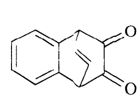
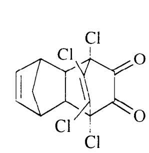
Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, 254 nm	 (70) + CO	1381
	UV	 → *ene* dimer (—) + CO	1382
	UV	 (—) + CO	1383
	UV	 (—) + CO	1383
	UV	 (≥ 32) + CO	1384
	180°, or UV	 (51) + CO	508
	220°, or UV	 Cond (%): 220° —; UV 95 + CO	1359, 1385
	UV	 (43) + CO	1359
	155° $t_{1/2}$ *ca.* 52 h	 (—) + CO + CP	284
	UV (brief)	 (—) + CP + CO	284
	UV	 (—) +  + CO	284
	UV	 (65) + CO	1386

TABLE XIV. KETENES AND RELATED ALKENES (*Continued*)

Starting Material	Conditions	Product(s) and Yield(s) (%)	Refs.
	UV, direct or sensitized	 (92 - 100)	1387
	UV, direct or sensitized	 12 - 18) +  (22 - 27) +  (12)	1387
	350°, or UV	($C_{14}H_{0}$ + $(C_{14}H_{10})_2$) Cond (%): 350° —; UV 100 + CO	1359
	UV	 (89) + CO	608

[a] *cis/trans* Is about 32/68 for this product.

[b] Analogous cyclobutanedione products occur with ,  and . No details are provided.

References

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3. Ichihara, A. Synthesis 1987, 207; rDA in Natural Product Syntheses.
4. Kwart, H.; King, K. Chem. Rev. 1968, **68**, 415; The Reverse DA or Retrodiene Reaction; includes chelotropic reactions as rDA; incorporates Woodward-Hoffmann rule discussion, relatively new at the time.
5. Lasne, M. C.; Ripoll, J. L. Synthesis 1985, 121; general review including methodology (FVP technique).
6. Ripoll, J. L.; Rouessac, A.; Rouessac, F. Tetrahedron 1978, **34**, 19; Recent Applications of rDA Reactions in Synthesis (in French).
7. Sweger, R. W.; Czarnik, A. W. in *Comprehensive Organic Synthesis*, Trost, B. M.; Fleming, I., Eds.; Pergamon Press, Oxford, 1991, Vol. **5**, Chapter "4.3" rDA Reactions; focus is synthetic applications, arranged by product of interest.

Historical & General Interest

8. Berson, J. A. Tetrahedron 1992, **48**, 3; Discoveries Missed, Discoveries Made: Creativity, Influence, and Fame in Chemistry.
9. Harries, C.; Gottlob, K. Justus Liebigs Ann. Chem. 1911, **383**, 228; see also: Harries, C. Justus Liebigs Ann. Chem. 1911, **383**, 157; prep. of isoprene by thermolysis of terpenes, and design of hot electrical wire “isoprene lamp”.
10. Japp, F. R.; Burton, C. I. J. Chem. Soc. 1887, **51**, 425; although the structures were not completely known at the time, the authors describe the formation and dimerization of 3,4-diphenylcyclopentadienone, followed by extrusion of CO from the dimer. These constitute the earliest examples of what we now recognize as DA and chelotropic reactions.
11. Schmidt, O. Zeitschrift Phys. Chem., A 1932, **159A**, 345; hydrocarbon cracking; notes strengthening of bond α to, and weakening of bond β to, double bond, and cites Staudinger's terpene work and pyrolysis of cyclohexene (both “rDA”) examples.
12. Schmidt, O. Chem. Rev. 1935, **17**, 140; Mechanism of Some Important

Organic Reactions; uses four examples of “rDA” reactions, to illustrate alternating bond strength principle.

13. Staudinger, H.; Klever, H. W. Chem. Ber. 1911, **44**, 2212; both “DA” and “rDA” reactions are clearly depicted in this paper; hot Pt wire/ N_2 flow was used to convert limonene to isoprene; correct structures are shown, and reversibility is noted; extension to other cyclohexenes is suggested.

Methodology

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General & Specific DA Reactions

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25. Afarinkia, K.; Vinader, V.; Nelson, T. D.; Posner, G. H. Tetrahedron 1992, **48**, 9111; DA Cycloadditions of 2-Pyrones and 2-Pyridones; the term “extrusion” is used to distinguish loss of CO_2 and RNCO from simple reversal of the DA reaction used to form the cycloadduct; a very

useful recent review.

26. Alder, K. *Neuere Methoden der Preparativen Organischen Chemie*, Verlag Chemie, Weinheim, Germany; 1943, Vol. **1**, pp. 251–358; includes discussion of problem that reversibility causes in some DA reactions, and suggests ways to avoid the problem (increase reactant conc., use of solvent in which cycloadduct is insoluble).
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MS independent of stereochemistry, therefore probably stepwise.

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68. Berson, J. A.; Olin, S. S.; Petrillo, E. W. Jr.; Bickart, P. Tetrahedron 1974, **30**, 1639; Stereo-chemistry and Mechanism of the [s2 + s2 + s2] Cycloreversion.

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