

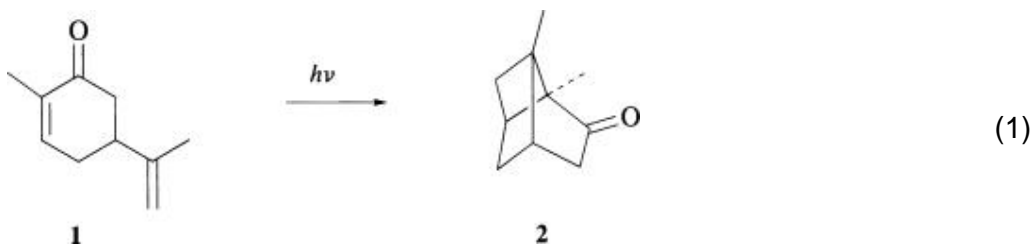
Enone Olefin [2 + 2] Photochemical Cycloadditions

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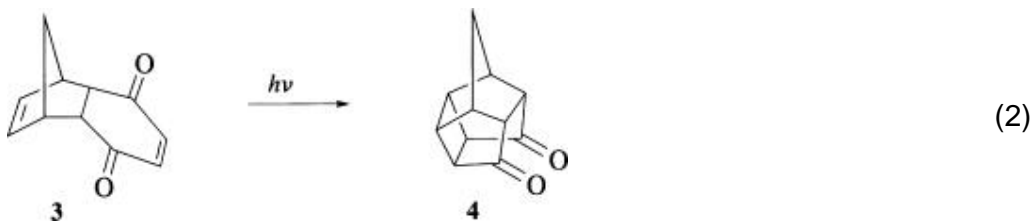
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1. Introduction

The photochemical [2 + 2] cycloaddition reaction of alkenes to enones, the light-induced cycloaddition of an excited state enone to a ground state alkene to produce a cyclobutane, is a highly useful reaction in organic synthesis since two new carbon-carbon bonds are formed and a maximum of four new stereogenic centers are introduced into the molecule in the process. (1-20) The first [2 + 2] photocycloaddition reaction was reported by Ciamician in 1908 when he observed the formation of carvone camphor (**2**) on exposure of carvone (**1**) to sunlight for one year (Eq. 1). (21)

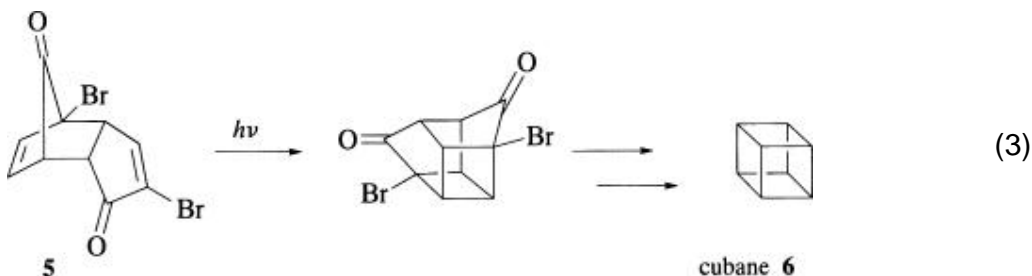


After confirmation of this finding (22) in the late 1950s numerous investigators immediately recognized the value of the reaction for the rapid construction of complex molecular frameworks. The photocycloaddition of a series of Diels-Alder adducts of various dienes and benzoquinones to efficiently produce complex caged structures was subsequently carried out. This included the cycloaddition of diketone **3** to form diketone **4** (Eq. 2). (23) Meanwhile, a similar photochemical cycloaddition of



enone **5** was utilized in a synthesis of the platonic solid cubane **6** (Eq. 3). (24, 25) Shortly thereafter investigations of the intermolecular reaction were

initiated through a study of the dimerization of cyclopentenone and the photocycloaddition of cyclopentenone to cyclopentene. (26, 27)



Further investigation of the various synthetic and mechanistic aspects of the photocycloaddition (3, 28-30) resulted in several total syntheses, including caryophyllene (31) and bourbonene, (32) as well as a proposed mechanistic rationale for the reaction. (33) As a result of this pioneering work, largely by Eaton, Corey, and De Mayo, numerous natural and nonnatural products have been prepared by synthetic routes which have a [2 + 2] photocycloaddition as a crucial step in their synthesis. Through further refining over the last 15–20 years, the photocycloaddition reaction has become recognized as an important transformation in the repertoire of the synthetic organic chemist.

Both the intermolecular and intramolecular versions of the reaction have been extensively studied. The intramolecular photocycloaddition, like the intramolecular variation of many reactions, has been the subject of much recent work. It is generally thought to be more predictable with regard to regiochemical and stereochemical control, but as will be seen from many of the examples in this chapter, the intermolecular reaction can be highly selective and predictable if the proper reaction participants and conditions are chosen.

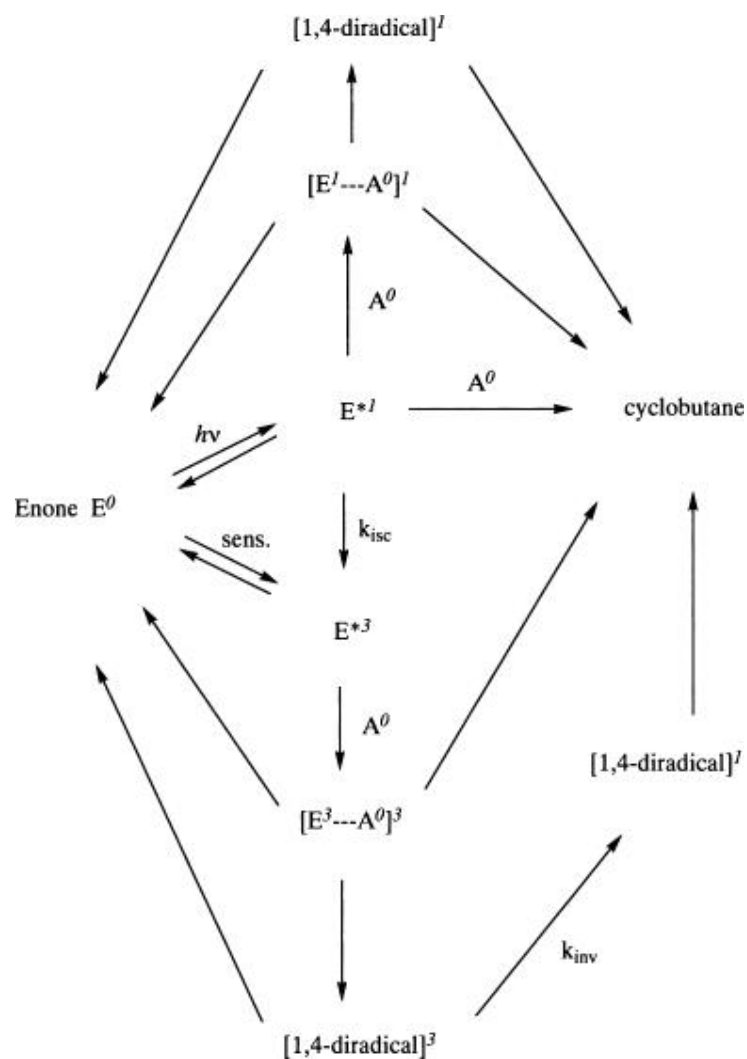
This chapter reviews the literature on the enone olefin [2 + 2] photocycloaddition since its discovery. Because of the volume of work in the field, there will undoubtedly be some omissions. Examples of all the major types of enone alkene photocycloadditions have been included so that the reader can get a sense of the historical evolution and the current state of the art. Both the *intermolecular* and the *intramolecular* variants of this reaction are treated in this chapter. The reader is also referred to a number of excellent reviews on the *intermolecular* reaction, the *intramolecular* reaction, and complete treatments which have appeared. (1-20)

2. Mechanism

Despite a number of extensive and elegant studies, many details of the [2 + 2] photocycloaddition reaction remain to be elucidated. This is at least partially attributable to the lack of a uniform mechanistic process for the reaction. It is apparent that the mechanism of the reaction varies depending on the substrate and the experimental conditions of the particular reaction.

Despite this lack of uniformity, several general points lead to a working hypothesis (Scheme 1) (7, 28, 31, 34) that serves as a basis for making rational predictions regarding the regiochemical and stereochemical outcome of many photocycloadditions. A basic understanding of these points is important to the synthetic chemist who wishes to utilize the reaction.

Scheme 1.



Absorption of a photon by the ground state enone E^0 normally produces the excited singlet E^{*1} (either $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$) (35-37) which can proceed by

various paths. It can (1) combine with a ground state alkene A^0 to form a singlet exciplex $[E^* \dots A^0]^1$, (2) intersystem cross to an excited triplet E^{*3} , or (3) relax back to the ground state. The singlet exciplex can decay back to the ground state, generate a cyclobutane directly, or produce a 1,4 diradical which can also collapse to the ground state or proceed to a cyclobutane. The most common productive path for the singlet is the conversion to a triplet state since intersystem crossing, particularly in five- and six-membered cyclic enones, is an efficient process. However, the singlet is relatively short lived in enone systems and decay back to the ground state will occur if *cis-trans* isomerization can take place. (38)

The triplet E^{*3} , which can result from the singlet E^{*1} or directly from sensitized excitation of the ground state E^0 , can either decay to the ground state or combine with a ground state alkene to generate a triplet exciplex $[E^* \dots A^0]^3$. (6) The exciplex can then form a carbon-carbon bond and produce a triplet 1,4-diradical which must undergo spin inversion to the singlet diradical before ring closure to the cyclobutane can occur. (39, 40) Additionally, at any point along the path to cyclobutane [i.e., (1) the triplet exciplex $[E^* \dots A^0]^3$, (2) the triplet diradical, or (3) the singlet diradical] the ground state alkenes can be regenerated. While exciplexes are useful in rationalizing the regiochemistry of some photocycloadditions, their existence is merely inferred. Indeed, a recent study by Schuster provides kinetic evidence which is inconsistent with exciplex formation. (41)

A general working mechanistic scheme which covers the majority of enone olefin photocycloadditions involves excitation to a short-lived singlet E^{*1} followed by intersystem crossing to the longer lived triplet E^{*3} . The triplet then forms an exciplex with the ground state alkene and the exciplex collapses to a triplet diradical. The triplet diradical spin inverts to the singlet and closes to the cyclobutane. If the initial excited singlet can undergo bond rotation, energy-wasting *cis-trans* isomerization will compete with intersystem crossing and subsequent photocycloaddition. This occurs primarily in acyclic systems that are not rigidly held by hydrogen bonding or in cyclic systems in which the carbon-carbon double bond is contained in a ring that is larger than a cyclohexane. (42)

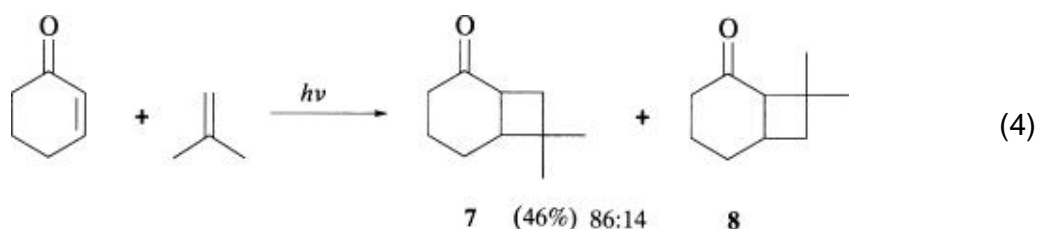
3. Scope and Limitations

3.1. Intermolecular Photocycloadditions

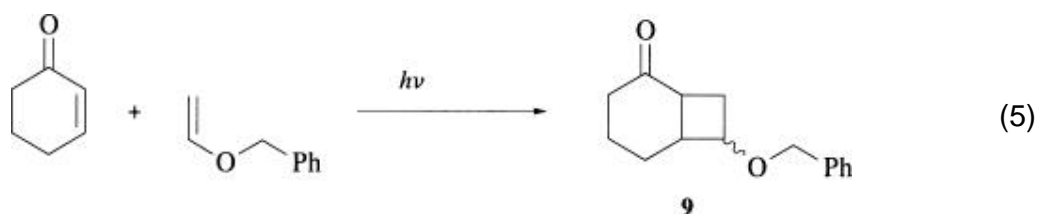
3.1.1.1. Regiochemistry

Regiochemical control of the intermolecular photocycloaddition is probably the most critical aspect of the reaction from the standpoint of synthetic utility.

When an unsymmetrical enone and an unsymmetrical alkene undergo a [2 + 2] photocycloaddition, two possible regiochemical isomers, the head-to-head and head-to-tail isomers, can result. The head of the enone is the carbonyl end, while the head of the alkene is generally the more highly substituted end or the end with the substituent of highest priority. For instance, when cyclohexenone is irradiated in the presence of isobutylene, a 4:1 mixture of the head-to-tail (HT):head-to-head (HH) products (**7**:**8**) is produced (Eq. 4). (28) The ratio of the isomeric photoadducts

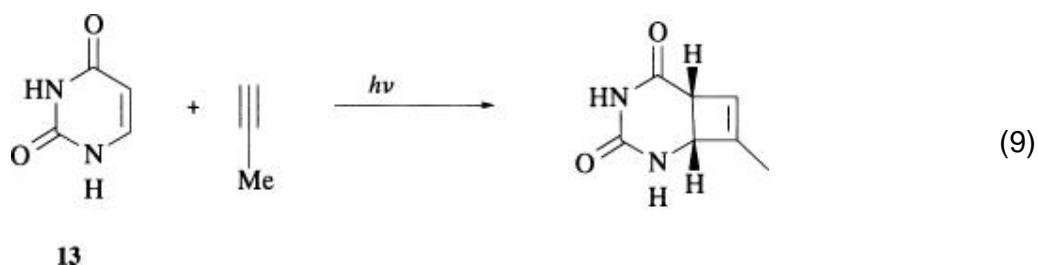
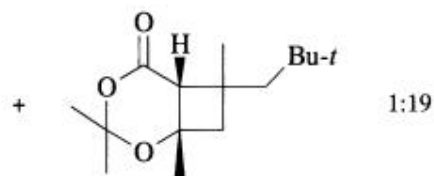
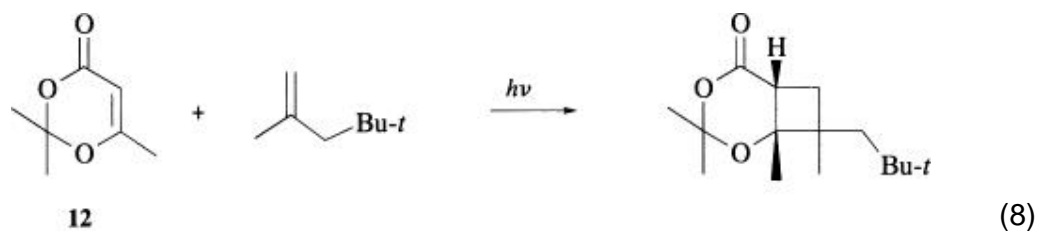
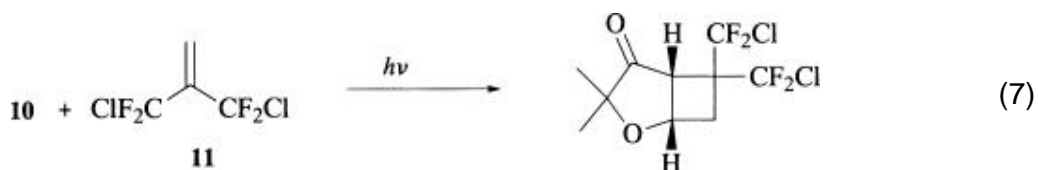
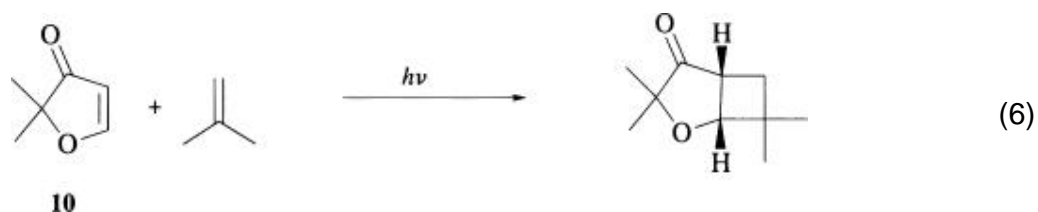


is generally thought to be controlled by electronic interactions in the excited state complex as well as steric interactions between the substituents on the two double bonds. The charge distribution of the excited enone is the opposite of its ground state configuration, and thus the enone β -carbon bears a partial negative charge. (28, 43, 44) During exciplex formation, the ground state alkene and the excited state enone are oriented to maximize electrostatic interactions. This is referred to as the polar exciplex theory. Consequently, a more highly polarized alkene such as benzyl vinyl ether can result in a single photoadduct **9** (Eq. 5). (28) A striking illustration

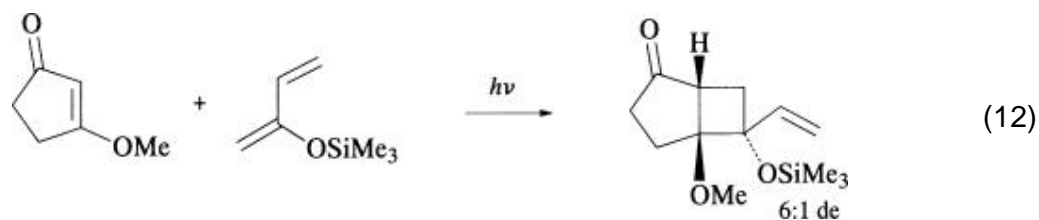
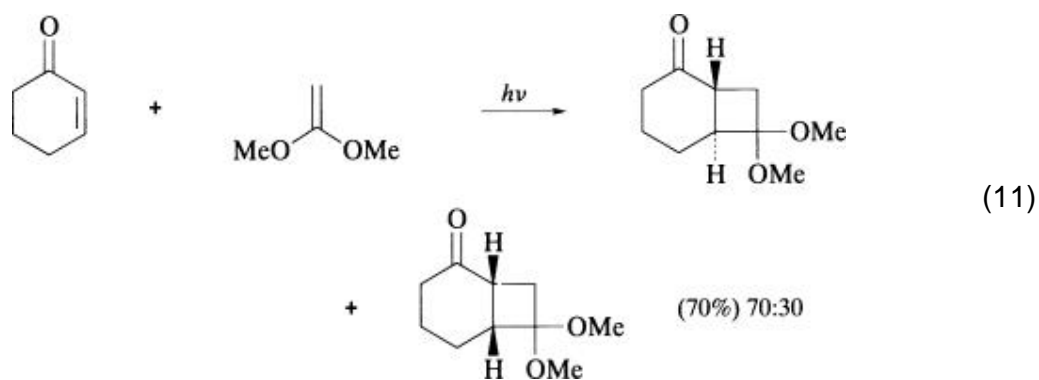
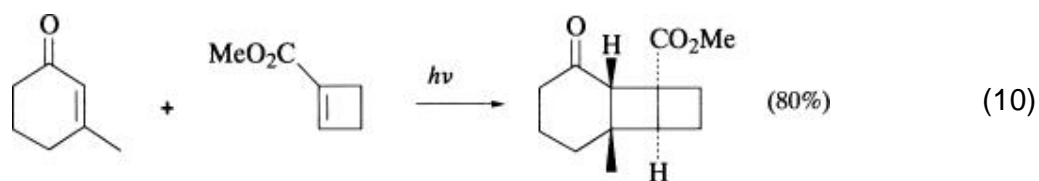


of how alkene polarization can affect regioselectivity is shown in the photoaddition of oxanone **10** to isobutylene (45-47) and the halogenated alkene **11** (Eqs. 6 and 7). (45) The change in polarity of the alkene causes a complete reversal of regioselectivity. Other highly polarized enones such as

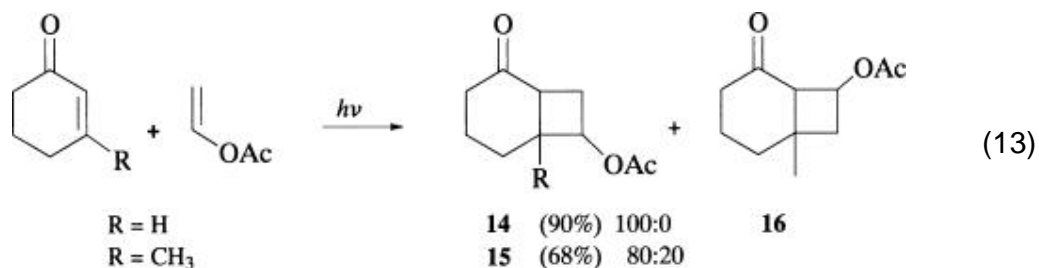
oxaenone **12** (48) and uracil (**13**) (49) also undergo highly regioselective photocycloadditions with a variety of alkenes (Eqs. 8 and 9).



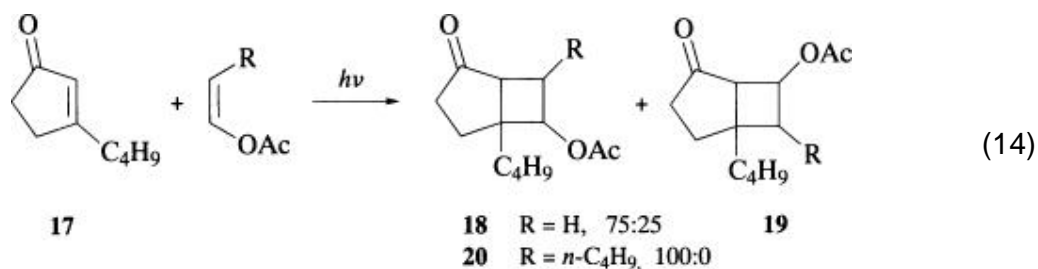
Other examples are shown in Eqs. 10–12. (28, 50-53) While this electrostatic interpretation can be a useful predictive tool, regioselectivity may be greatly influenced by the rate at which each initially formed exciplex or 1,4-diradical proceeds to products or reverts to the ground state.



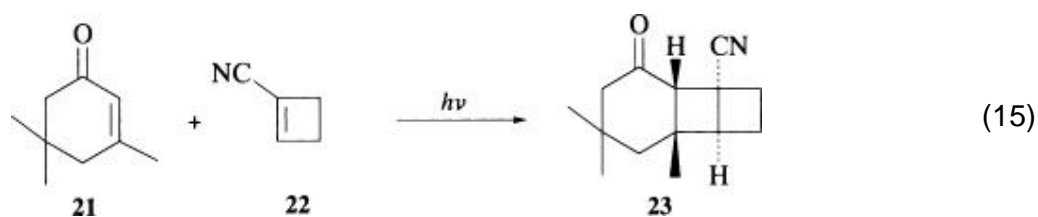
Steric interactions can also affect regioselectivity. Thus cyclohexenone reacts with vinyl acetate to give exclusively the head-to-tail regioisomer **14**, (54) while 3-methylcyclohexenone produces a 4:1 mixture of the head-to-tail:head-to-head isomers **15**:**16** (Eq. 13). (55) Photocycloaddition of 3-*n*-butylcyclopentenone (**17**) with



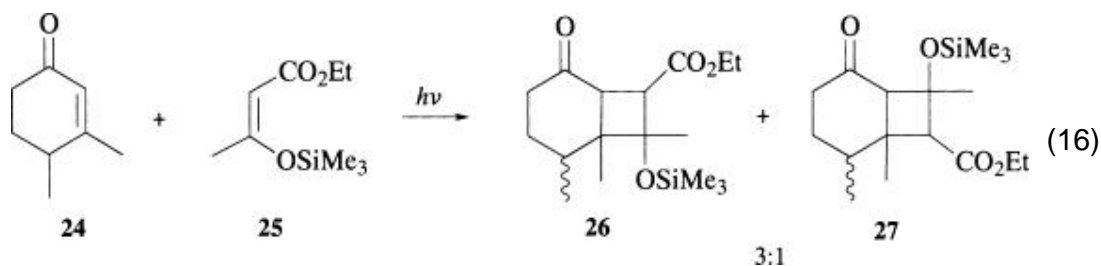
vinyl acetate gives a 3:1 mixture of head-to-tail:head-to-head photoadducts **18:19**, while 1-acetoxy-1-hexene gives exclusively the head-to-tail adduct **20** because of steric interaction between the two alkyl chains (Eq. 14). (56)



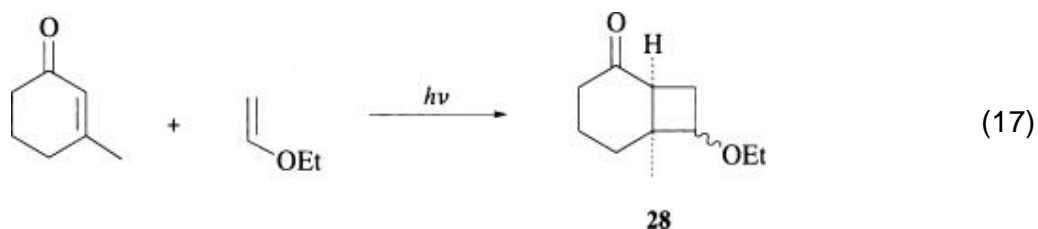
When steric and electronic effects influence the regiocontrol of a photocycloaddition in similar ways, the selectivity is very high as observed in the reaction of enone **21** with alkene **22**, which gives a single photoadduct **23** (Eq. 15). (57, 58)



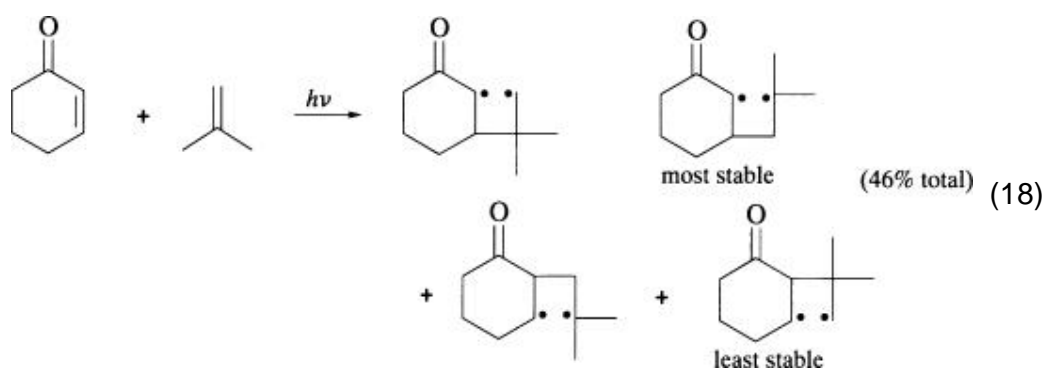
Conversely, selectivity suffers when the two effects counteract one another as in the photoaddition of enone **24** and alkene **25**, which produces a 3:1 mixture of regioisomers **26:27** (Eq. 16). (59) In many instances where steric effects are minimal, a



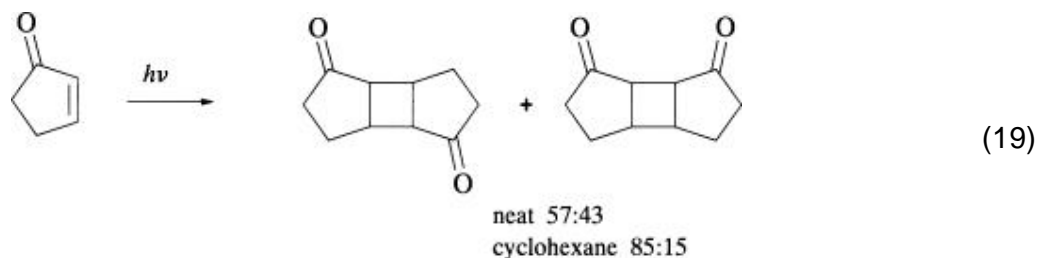
strong electronic preference for one regioisomer controls the outcome of the reaction as in the formation of cyclobutane **28** from 3-methylcyclohexenone and ethyl vinyl ether (Eq. 17). (60)



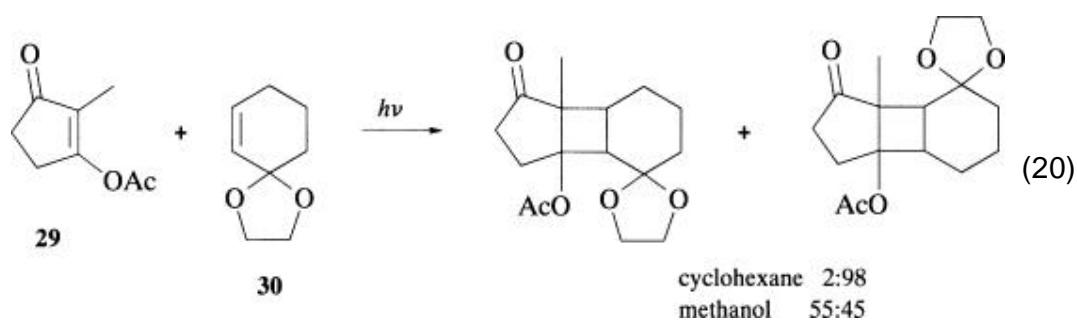
Regioselectivity has also been attributed to the production and partitioning of various 1,4-diradicals. (4) While the product ratio may clearly depend in some instances on the rates of partitioning of the diradicals to cyclobutane versus ground state alkenes, it is difficult to determine relative partitioning rates of diradicals. Overall, the polar exciplex theory, in combination with the consideration of steric interactions, serves as a useful model for predicting regioselectivity in most intermolecular photocycloadditions.



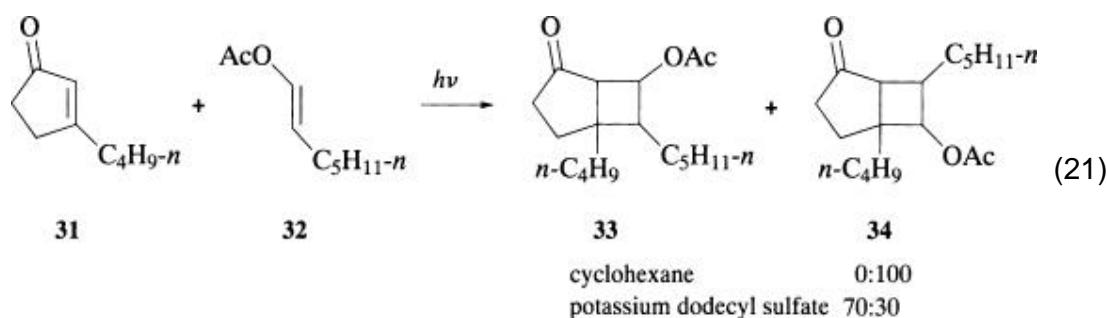
Choice of reaction parameters such as solvent and temperature can also be used to influence the regiochemical outcome of many photocycloadditions. The polar exciplex model would predict that solvent polarity can affect the regioselectivity of a photocycloaddition by influencing the charge transfer interaction in the exciplex. The dimerization of cyclopentenone (Eq. 19) results in a larger proportion of the



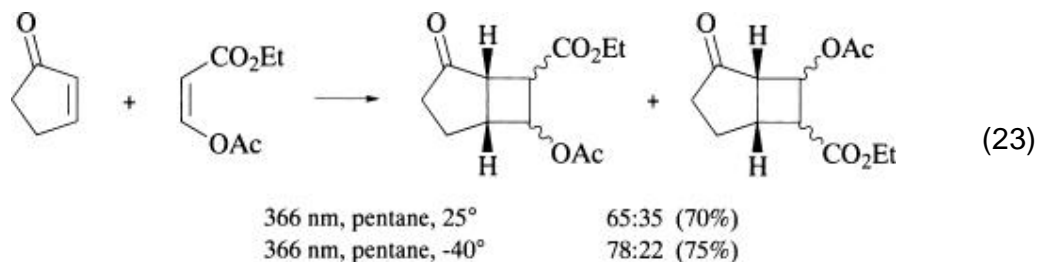
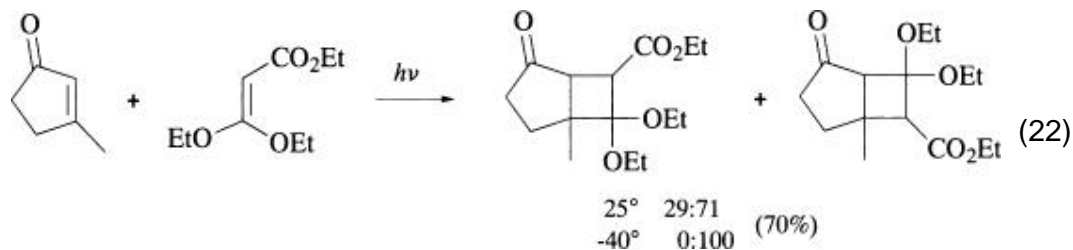
head-to-tail adduct in more polar solvents. (61-63) The photoaddition of enone **29** to alkene **30** also displays a pronounced solvent dependence. (64) Nonpolar solvents tend to produce products that would be predicted from the polar exciplex model, while more polar solvents tend to temper electrostatic interactions, resulting in a somewhat higher proportion of the minor product but generally not causing complete reversal of the regioselectivity.



Organized media can also influence the regiochemical outcome in photocycloaddition reactions. (56) Photoaddition of 3-*n*-butylcyclopentenone (**31**) with various terminal olefins shows a pronounced regioselectivity which reflects the alignment of the enone and the olefin with their polar groups toward the surface of a micelle. This effect is most pronounced with 1-acetoxy-1-heptene (**32**), which gives exclusively the head-to-tail adduct **34** in cyclohexane solvent but leads to a 2.3:1 predominance of the head-to-head isomer **33** in the presence of potassium dodecyl sulfate.



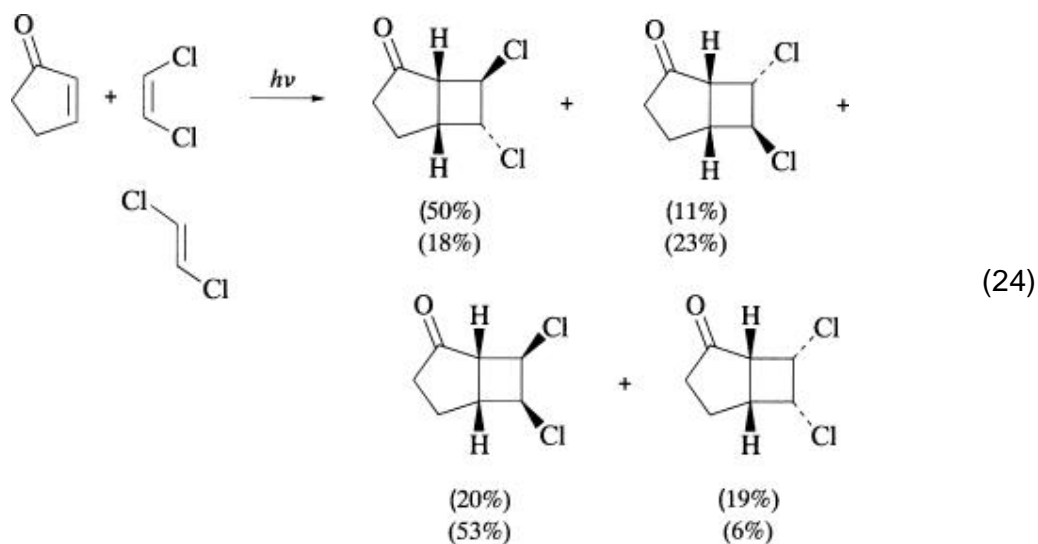
Varying the temperature of the photoaddition reaction can also produce minor changes in the regioselectivity. Typically, lowering the temperature tends to enhance the selectivity in favor of the major regioisomer as in the examples in Eqs. 22–23. (65)



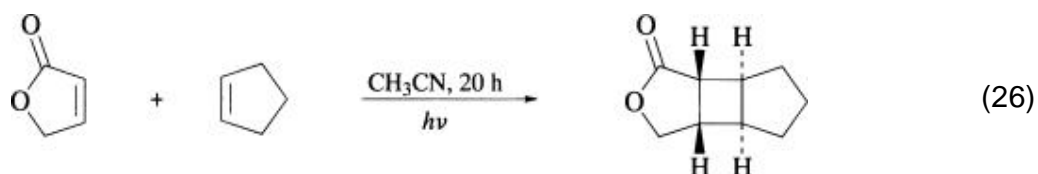
3.1.1.2. Stereochemical Control

Given that a maximum of four new stereogenic centers can be produced in a photocycloaddition reaction, stereocontrol and the predictability of stereochemical induction become extremely important when using [2 + 2] photoadditions in synthesis. Stereoisomerism in the products of photoaddition can result from (1) geometric isomers about the cyclobutane ring, (2) a preexisting stereogenic center on the alkene, (3) a preexisting stereogenic center on the enone, or (4) any combination of the first three.

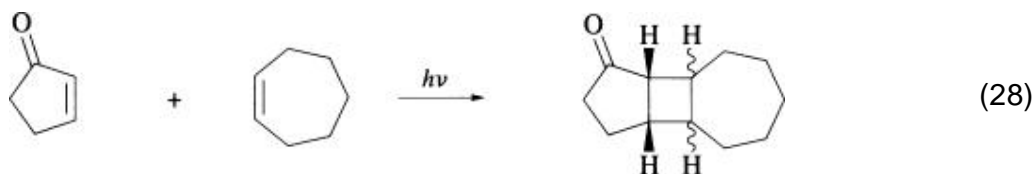
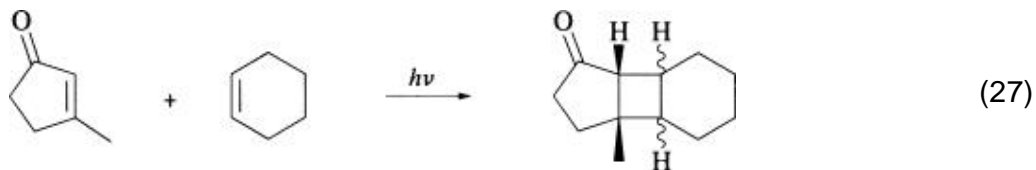
Let us first consider the question of geometry about the cyclobutane ring. Since the photocycloaddition is not concerted and proceeds through an intermediate 1,4-diradical, rotation about single bonds in the diradical can result in scrambling of alkene geometry if the alkene is acyclic or if the double bond is contained in a ring larger than six membered. As an illustration, irradiation of cyclohexenone in the presence of *cis*-2- or *trans*-2-butene furnishes the same mixture of three stereoisomeric photoadducts. (28) Similarly, cyclopentenone and 1,2-dichloroethene produces all four possible *cis* photoadducts when either the *cis* or *trans* alkene is used (Eq. 24). (40) In the latter reaction, the ratios of products are somewhat different depending on the geometry of the alkene; this may simply be a result of different rates of cyclobutane closure of the initially formed diradicals.



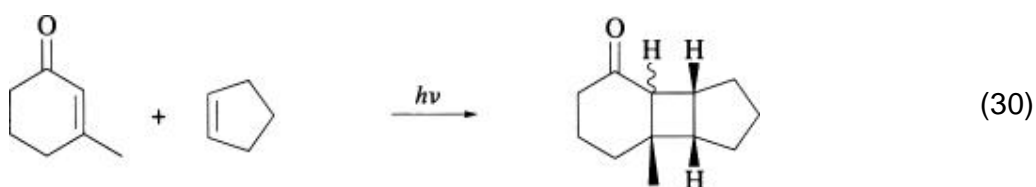
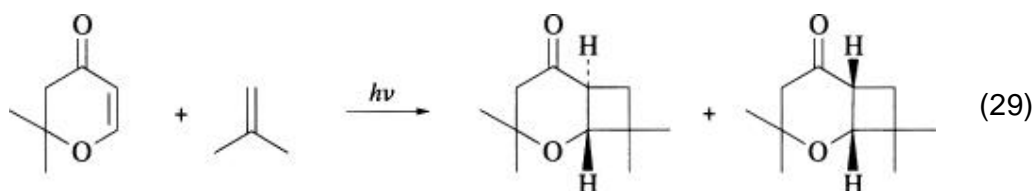
When cyclic alkenes which have ring sizes of five members or less are used as the alkene partner, the alkene geometry is preserved since *cis-trans* isomerization is inhibited (Eqs. 25–26). (66, 67) Use of larger rings, however, can result in loss of alkene



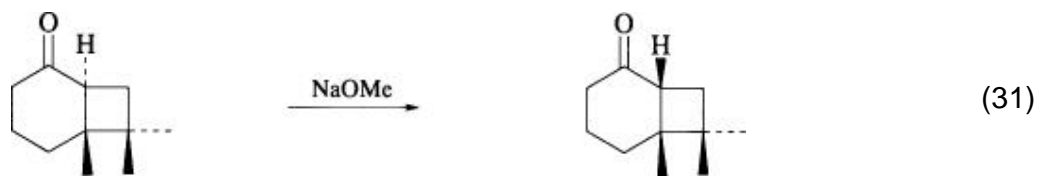
stereochemistry (Eqs. 27–28). (56, 68, 69) The cyclobutane ring juncture between the enone and the cyclobutane is always *cis* if the enone is contained in a five-membered



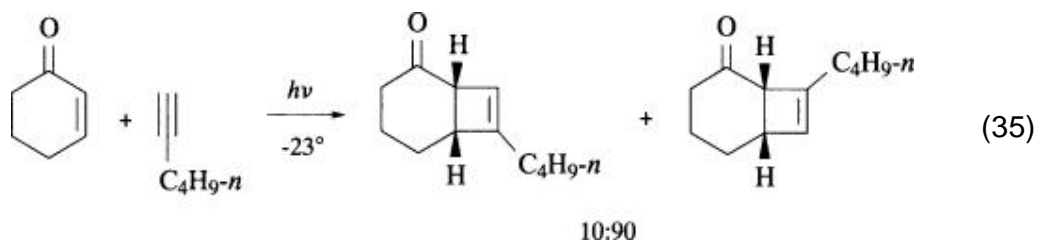
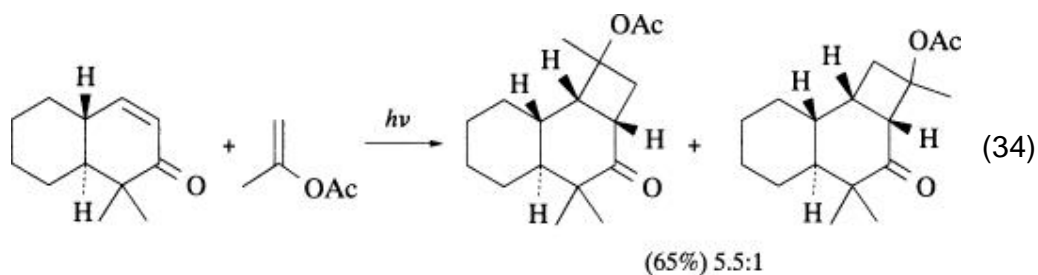
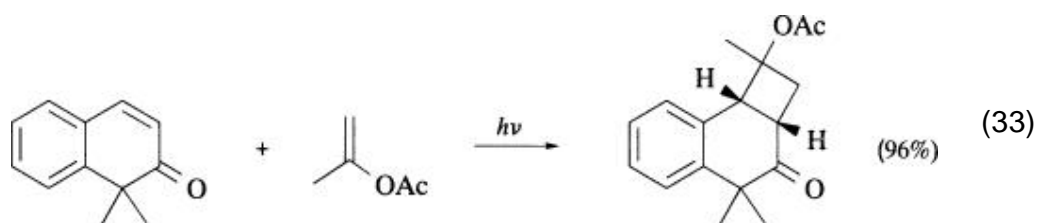
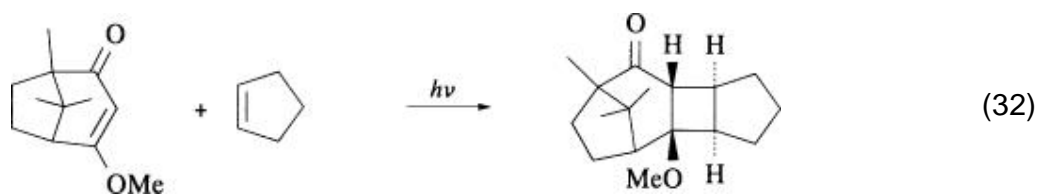
(or smaller) ring. Considerable strain would be introduced into the five-membered ring if the enone excited state were sufficiently twisted to allow formation of the *trans* isomer (Eqs. 6·21·27·28). (47, 56, 40, 68) However, cyclohexenones commonly produce significant amounts of *trans* products at the cyclohexane–cyclobutane ring juncture (Eqs. 11·29·30). (28, 70, 71) Spectroscopic evidence indicates

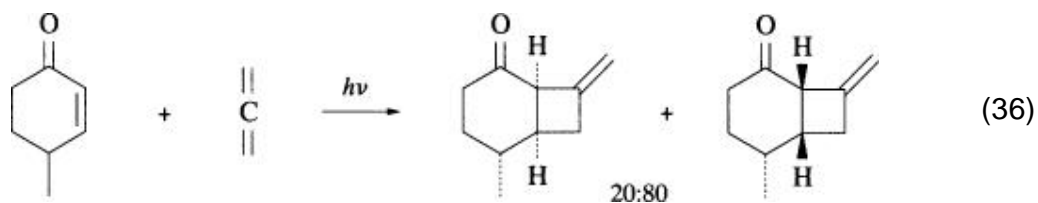


that some cyclohexenone triplets are substantially twisted about the carbon–carbon double bond, thereby permitting bond formation on one side of the ring at the α carbon and bond formation from the opposite face at the β carbon. (35, 36) Production of the *trans* isomer is normally of no consequence since the *trans* isomers are readily isomerized to the more stable *cis* diastereomers (Eq. 31). (28) This isomerization often



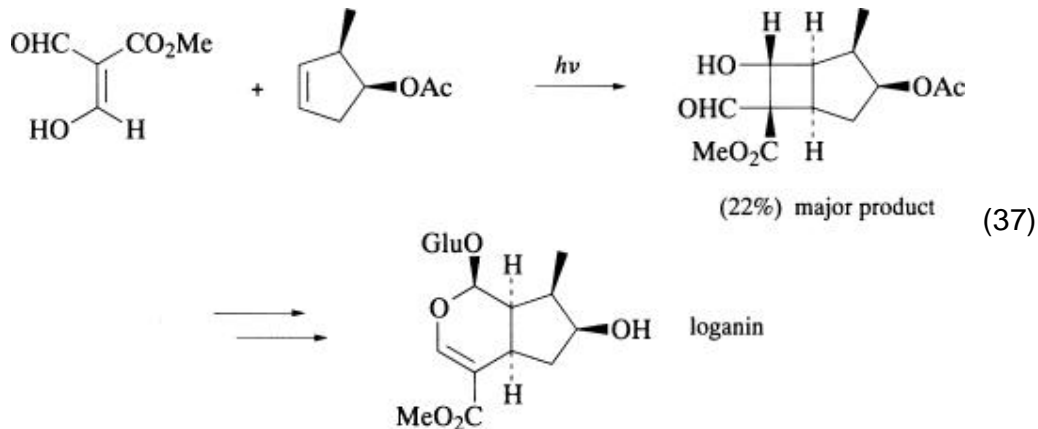
occurs spontaneously upon workup or chromatography. In addition, conformationally rigid cyclohexenones tend to produce predominantly or exclusively *cis* ring fusions (Eqs. 32–34). (55, 72, 73) The *cis* product is also obtained with cyclohexenones if the product cyclobutane has a high level of ring strain, for example with cyclobutenes, alkynes, or allenes as the ground state alkene (Eqs. 10, 35, 36). (50-52, 74, 75)

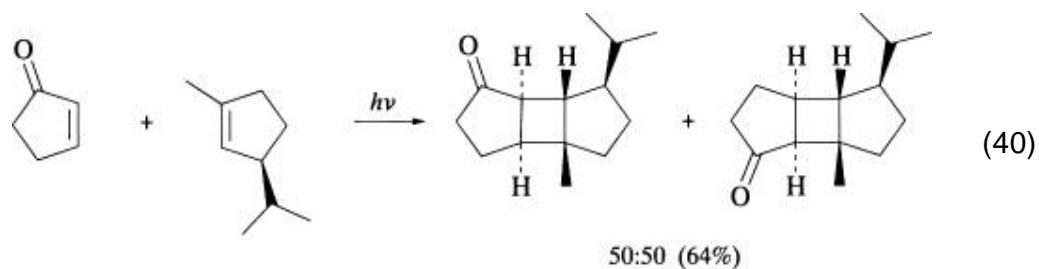
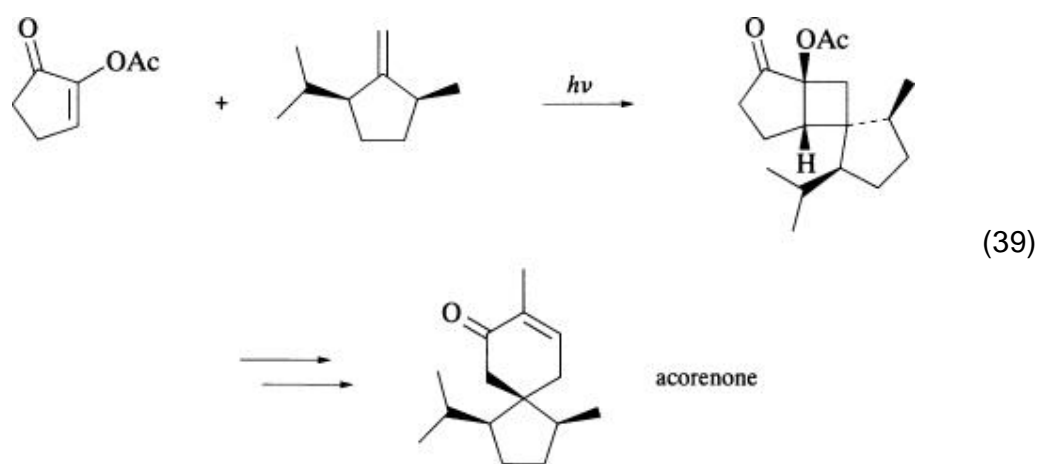
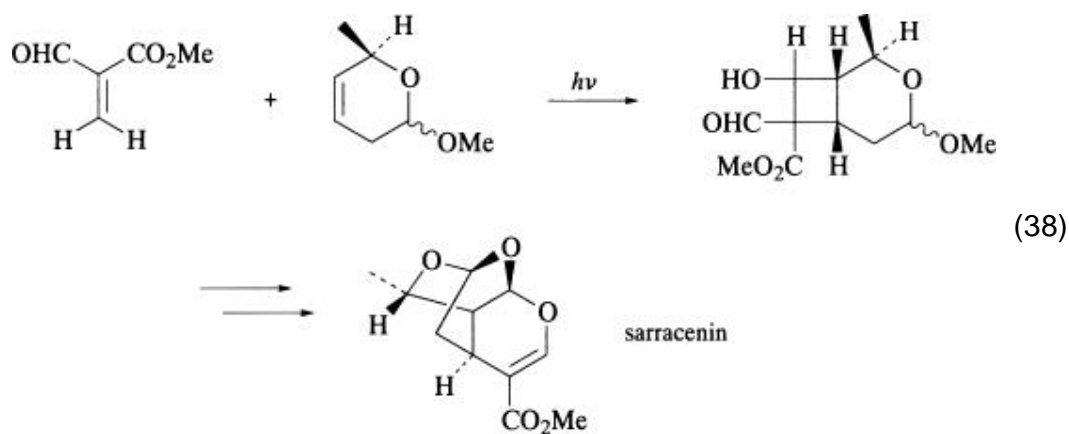




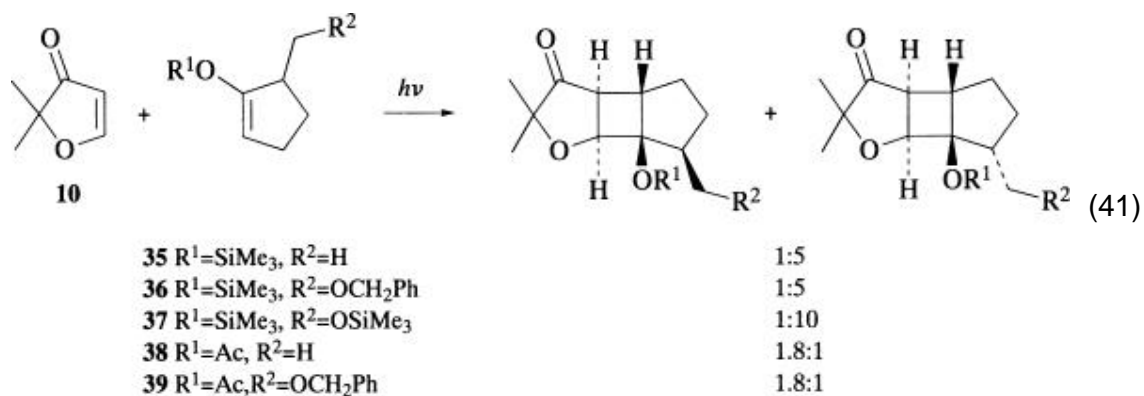
Facial selectivity, when possible, tends to favor the *exo* or *cis-anti-cis* geometry as can be seen in Eqs. 10, 15, 25, 26, and 32. This outcome is presumably a result of steric interactions between the alkene substituents and the enone ring carbons in the *cis-syn-cis* isomer.

The remaining stereochemical point that must be addressed is the effect of a preexisting stereogenic center on either the excited state enone or ground state alkene. Generally, a stereogenic center in the ground state alkene will influence the stereochemistry of the product in a predictable way. That is, the excited state enone normally adds to the sterically most accessible face of the ground state alkene as in the photoadditions in Eqs. 37–40. (76, 77-32)

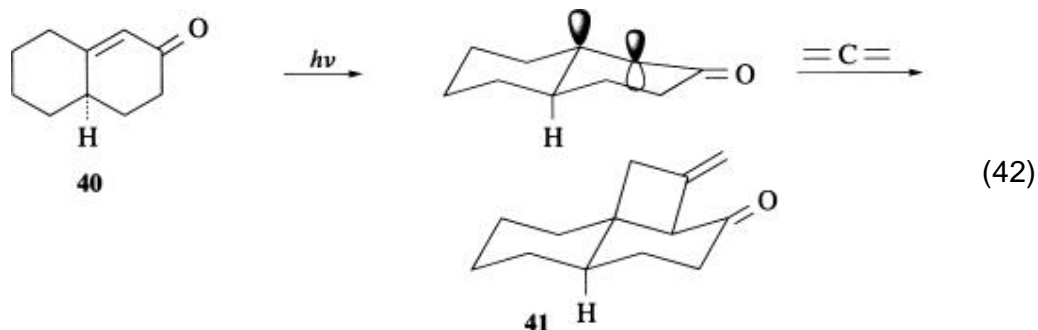




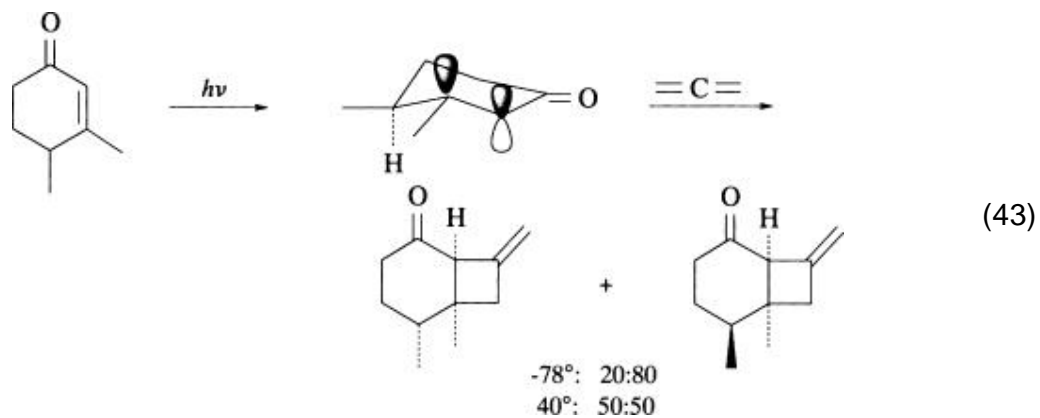
The addition of the dimethylfuranone **10** to enol derivatives **35–39** (Eq. 41) produces the product which would appear to result from approach to the more hindered face of the alkene. **(81)** This result can be rationalized by $A_{1,2}$ strain in the cyclopentene in a similar manner to the epoxidation of 1,5-dimethylcyclopentene. **(82)**



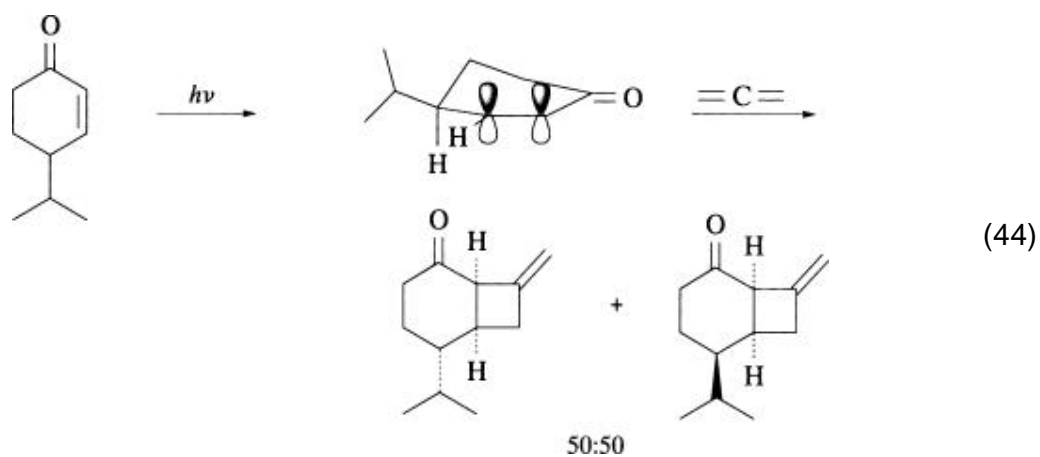
The effects of a resident stereogenic center on the excited state enone are less straightforward. One rationale that is particularly useful for cyclohexenones is based on attack of the ground state alkene on the most stable conformation of an excited state enone in which the β carbon is substantially pyramidalized. (83, 84) For example, addition of allene to octalone **40** produces **41**, which results from addition of allene opposite the angular substituent. (84) The stereochemical results in these photoadditions can be compared to similar results in dissolving metal reductions, such as in enone **40**. These reductions are also presumed to proceed through a species in which the

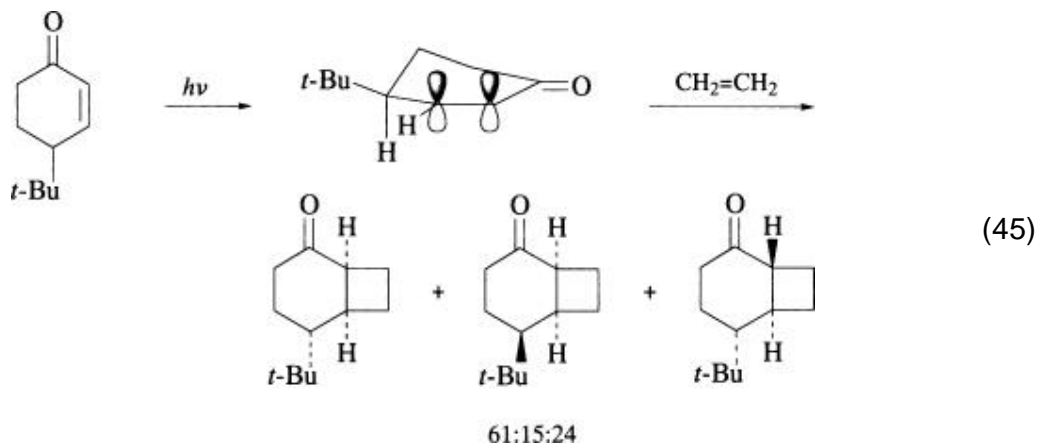


β carbon is pyramidalized. (85) The addition of allene to 3,4-dimethylcyclohexenone (Eq. 43) supports this model since the predicted product should arise from *cis*



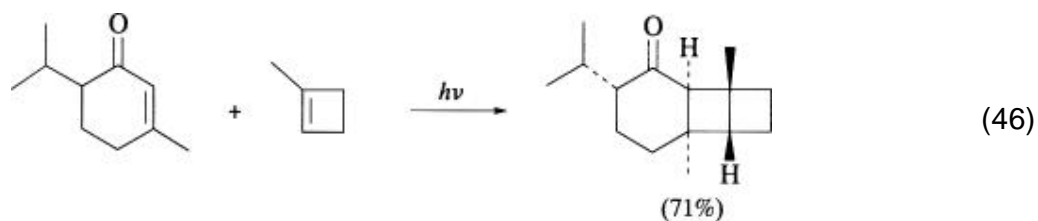
approach to the C(4) methyl. (75) Alternatively, $A_{1,2}$ strain, as in the epoxidation of 1,6-dimethylcyclohexene, could be the source of the stereocontrol. No selectivity is displayed in the photoaddition of 4-isopropylcyclohexenone to allene, (31, 86) whereas 4-*tert*-butylcyclohexenone yields the *trans* adduct as the major isomer, (87) albeit with ethylene as the ground state olefin (Eqs. 44 and 45).

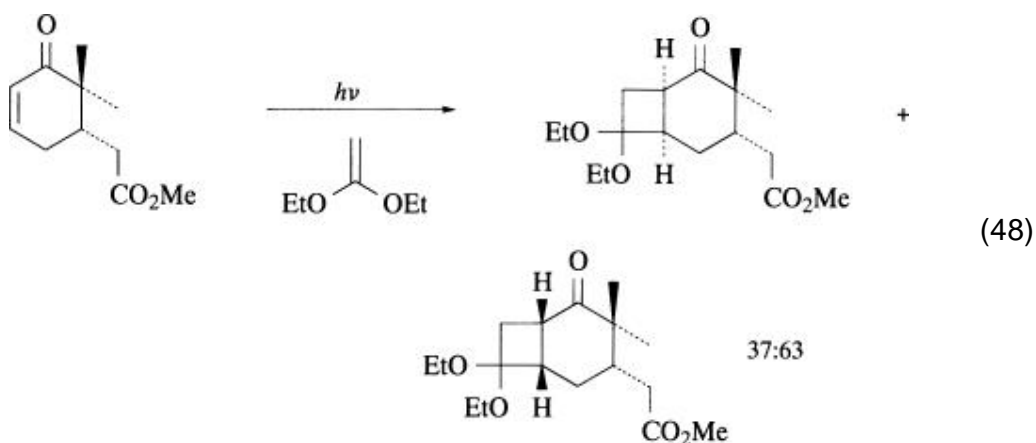
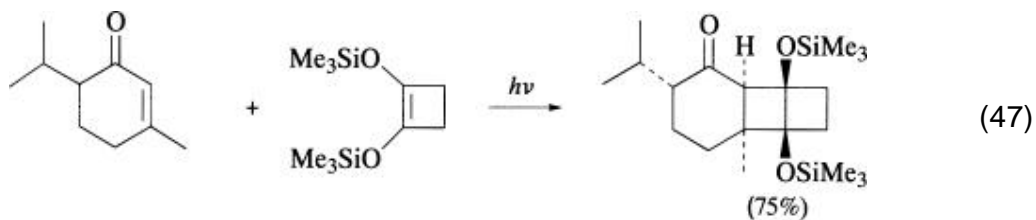




It would appear that some or all of the examples given above might be better rationalized as proceeding through an excited state with a trigonal β carbon, with pyramidalization occurring along the reaction coordinate with the ground state alkene. This agrees more closely with theory. Torsional strain induced in a conformation with a trigonal β carbon could explain such examples as 3,4-dimethylcyclohexenone (Eq. 43). It has also been proposed that photoadditions involving allenes as ground state olefins may be different mechanistically from those involving ordinary alkenes, at least in intramolecular cases. (88)

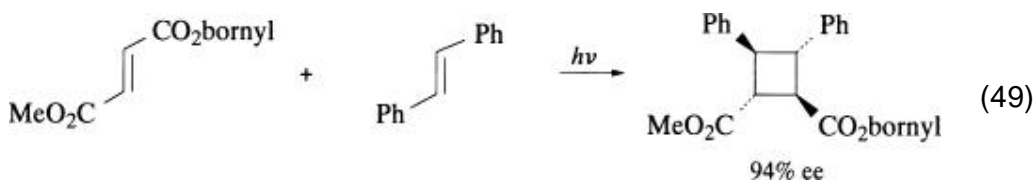
Cyclohexenones with substituents at the 5 and 6 positions tend to give the product that would be predicted by steric approach control to an excited state with a trigonal β carbon (Eqs. 46–48). (66, 89, 90) As a final cautionary note, while these hypotheses are often useful for prediction of stereochemical results, the true source of selectivity may involve rates of cleavage of the intermediate diradicals to ground state versus rates of cyclobutane ring closure. Insufficient data are currently available to explain completely these results.

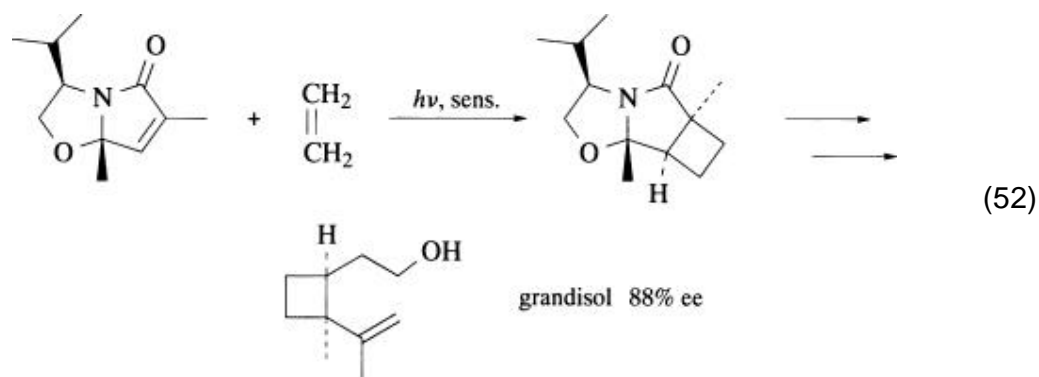
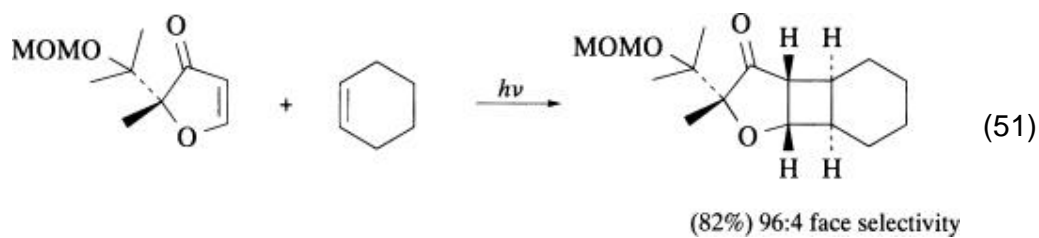
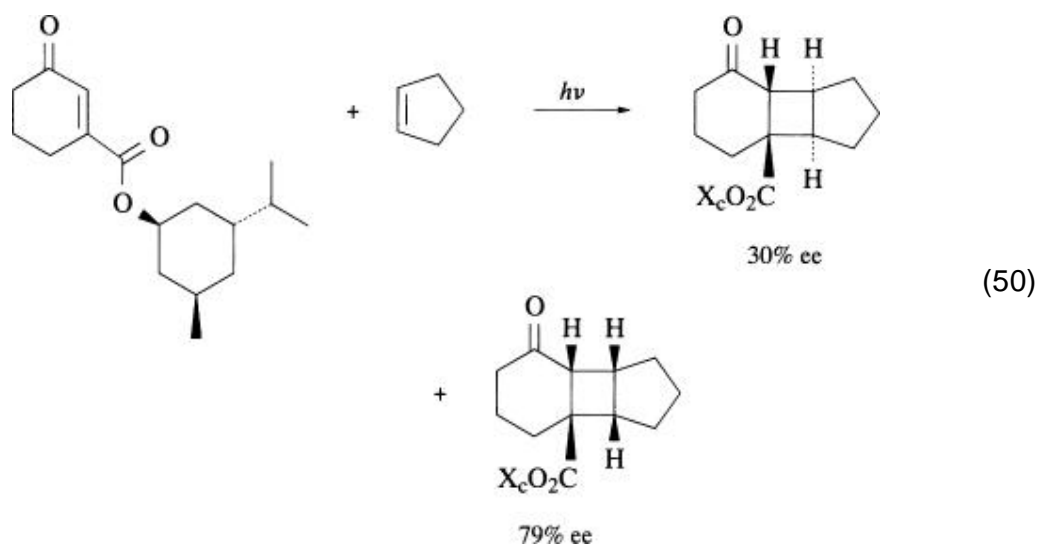




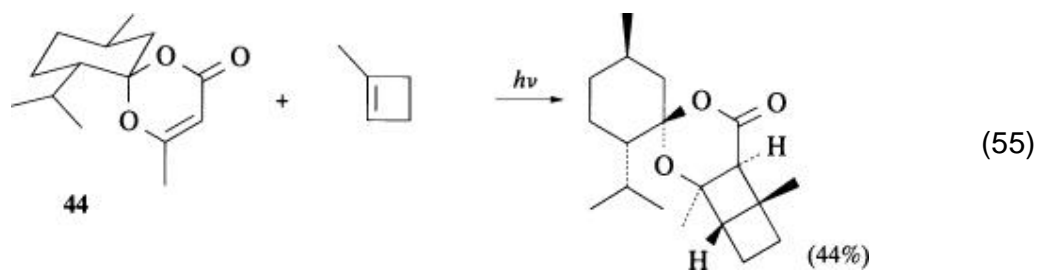
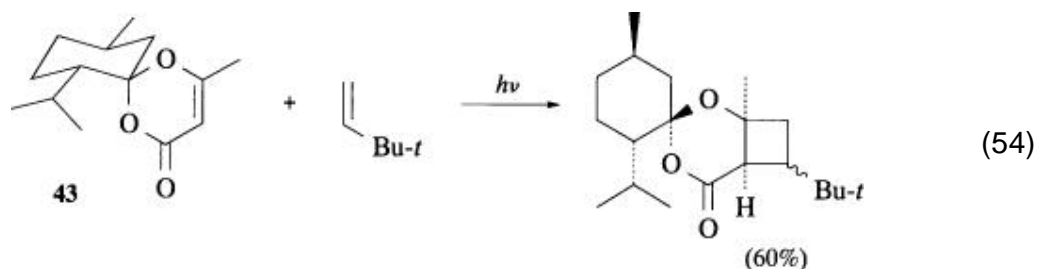
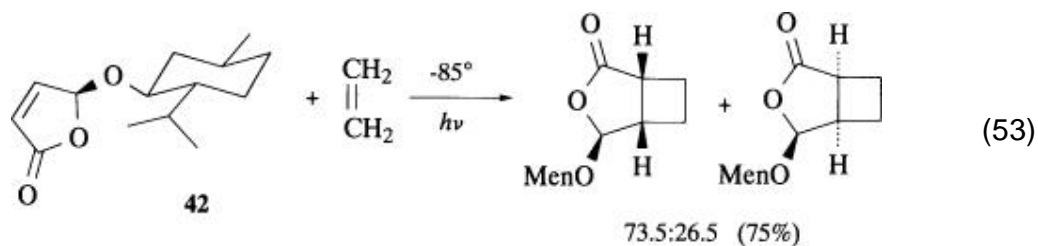
3.1.1.3. Enantioselectivity

Few reports have appeared regarding control of absolute asymmetry in photocycloadditions, despite recent advances in the field of asymmetric synthesis. The first example of the use of a “removable” chiral auxiliary is the photocycloaddition of bornyl fumarate to stilbenes to provide impressive enantioselectivity (Eq. 49). (91) More recently it has been shown that phenylmenthyl cyclohexenone carboxylates produce modest levels of absolute stereochemical control (Eq. 50). (92) Excellent facial selectivity is also possible in the photoaddition of compounds where the stereogenic center that controls diastereoselectivity can be excised to afford products of high enantiomeric purity (Eqs. 51 and 52). (93, 94) Substituted





lactone [42](#) ([95](#)) and sterically biased dioxolenones [43](#) ([96](#)) and [44](#) ([96](#)) also show promise for asymmetric syntheses based on [2 + 2] photocycloadditions (Eqs. [53–55](#)).



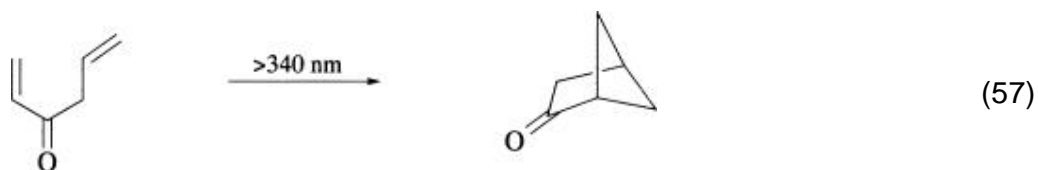
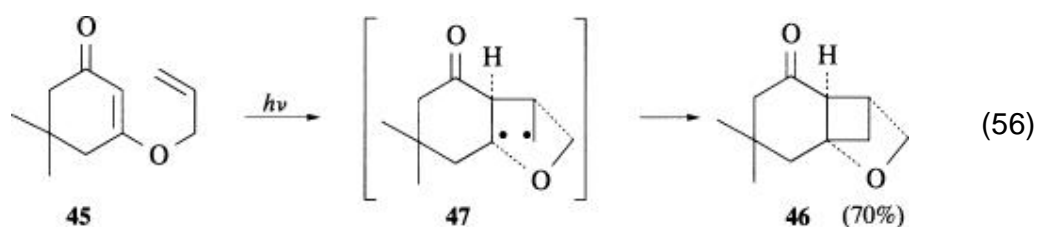
3.2. Intramolecular Photocycloadditions

Although many examples of the *intermolecular* photochemical [2 + 2] cycloaddition show high levels of regiochemical and stereochemical control, the numerous examples of reactions in which the regio and stereoselectivity is low or unpredictable have kept many researchers who are inexperienced in photochemistry from utilizing this important reaction. The low selectivity of many *intermolecular* photocycloadditions can be significantly improved if the enone and the alkene are part of the same molecule. The geometric constraints that are placed on intramolecular photocycloadditions can usually override the problems that lead to multiple products in the analogous intermolecular reaction. The excited state is also trapped more readily because of the proximity of the ground state alkene, generally improving the efficiency of the process and reducing nonproductive side reactions. While many of the early examples of [2 + 2] photocycloaddition were *intramolecular*, this variation of the reaction saw limited use in the synthesis of complex molecules until the 1970s, when its potential for the rapid construction of a wide array of complex polycyclic carbon skeletons was recognized.

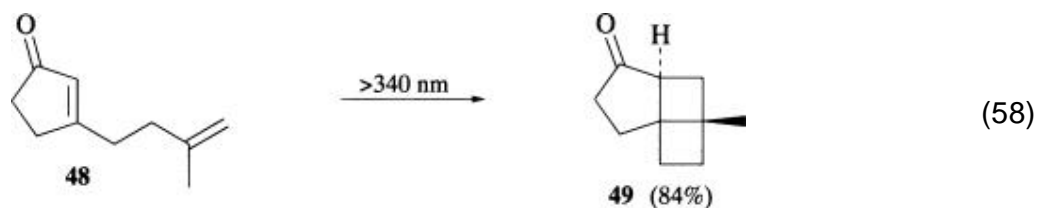
3.2.1.1. Regioselectivity

Kinetics of ring-forming reactions as well as geometric constraints on the transition state conformations in the initial and final cyclobutane ring closures contribute to the high levels of regiochemical control in intramolecular photocycloadditions. Since five-membered rings form faster, they are formed preferentially over six- or four-membered rings (this observation has been termed the “Rule of Fives”). (97, 98) Six-membered rings are preferred when five-membered ring formation is not possible. The preference for five-membered ring formation is analogous to the selective formation (75:1) of the cyclopentylmethyl radical over the cyclohexyl radical in the cyclization of the 5-hexenyl radical. (99) Thus when the enone and the olefin are connected by a tether of two, three, or four atoms, the regioselectivity is generally very high, often producing a single regioisomer.

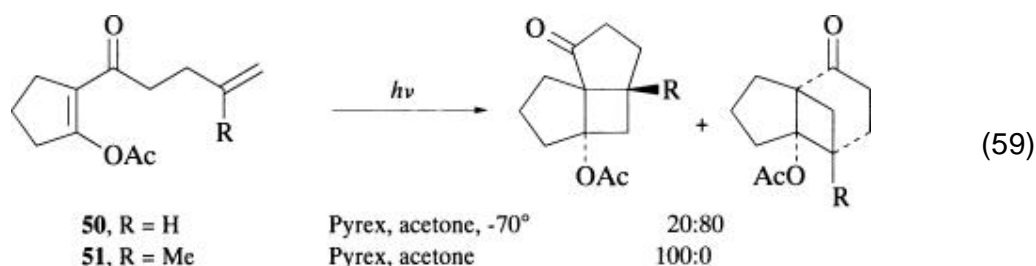
An example of a system with a two-atom tether, enone **45**, produces exclusively photoadduct **46** through initial formation of a five-membered ring to give the intermediate diradical **47** (Eq. 56). (100) Another example is illustrated in Eq. 57. (101, 102) This



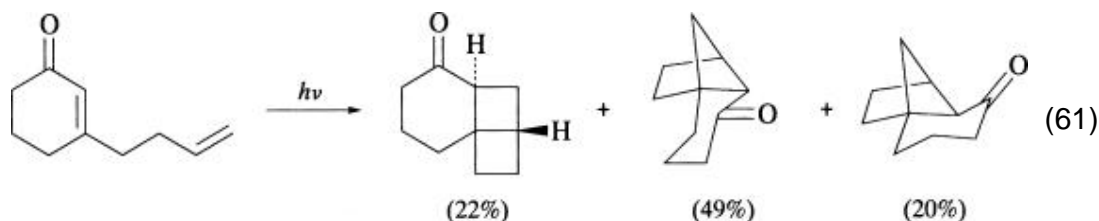
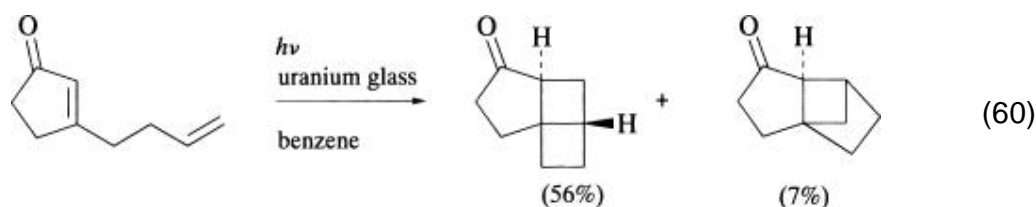
regioselectivity can be altered by substitution on the internal carbon of the ground state double bond. Enone **48** thus provides an 84% yield of cyclobutane **49**. (103-105)



This effect can be explained by a change in the mechanism: substitution on the internal carbon retards five-membered ring formation, and 1,6-cyclization predominates. This result is again similar to the effect seen when the 5-hexenyl radical is substituted at the same position. A similar result occurs when enone **50** and its analog **51** are irradiated. (106, 107) The photoaddition of the substituted alkene provides a higher proportion of the straight adduct. This effect has also been observed when the enone double bond of 1,5-hexadienes is constrained within a five- or

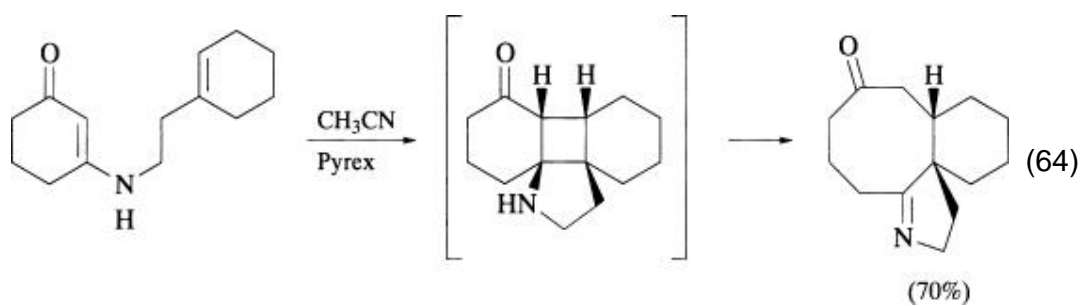
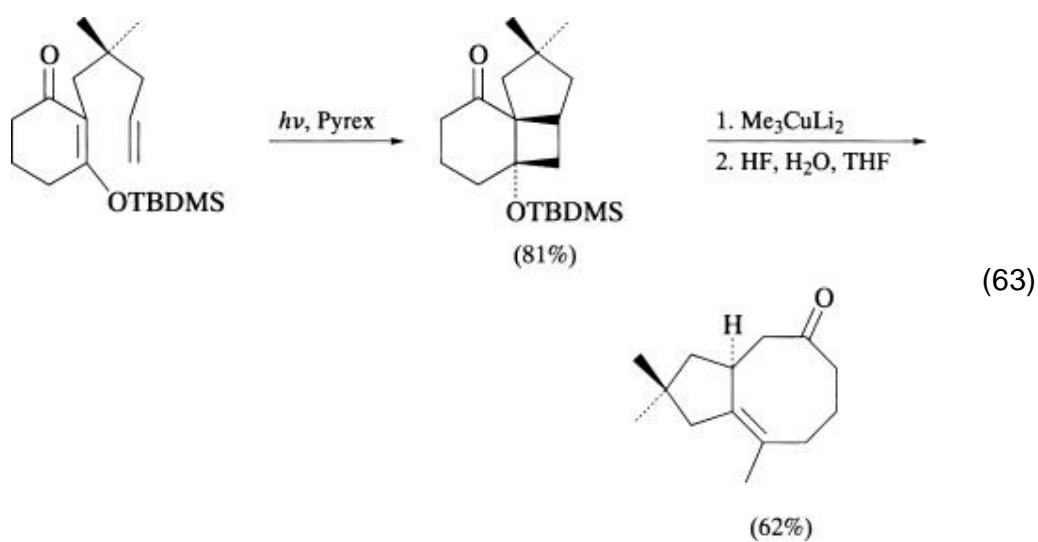
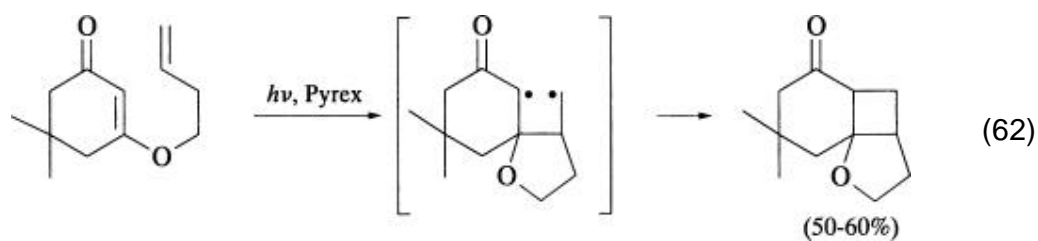


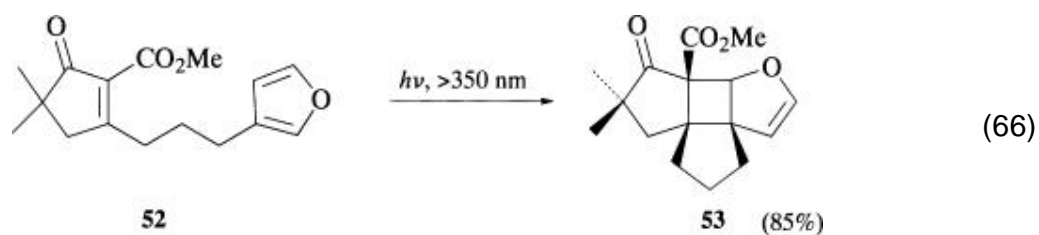
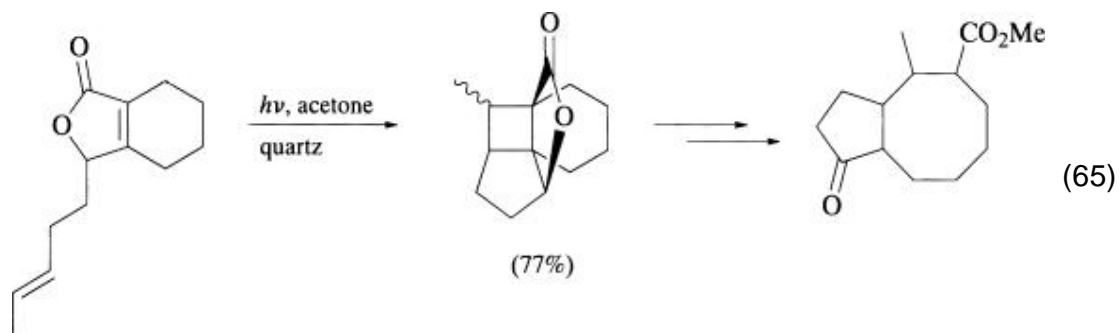
six-membered ring, as illustrated by comparing Eq. 57 with Eqs. 60 and 61. (103-105) When the enone is in a ring, twisting in the excited state is minimized, thereby reducing the amount of crossed adduct formed.



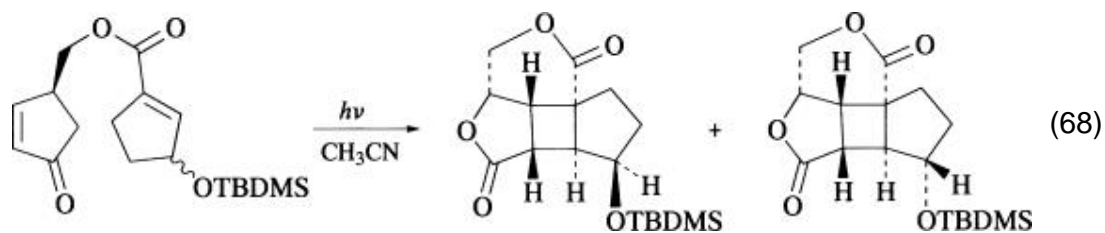
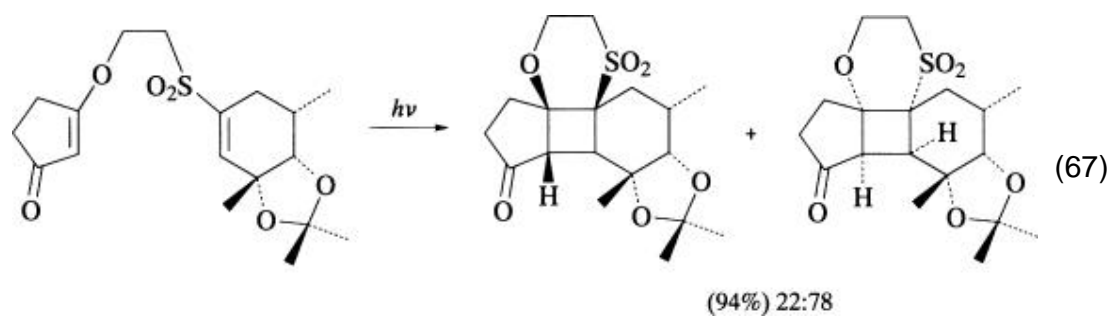
Systems with three-atom tethers display quite predictable regiochemical control, generally giving the straight adduct as the exclusive product through initial five-membered ring formation (Eqs. 62–65). (108-112) Cyclopentenone **52** is particularly illustrative since it contains a highly polarized enone and alkene and produces exclusively vinyl ether **53**, the opposite regioisomer that

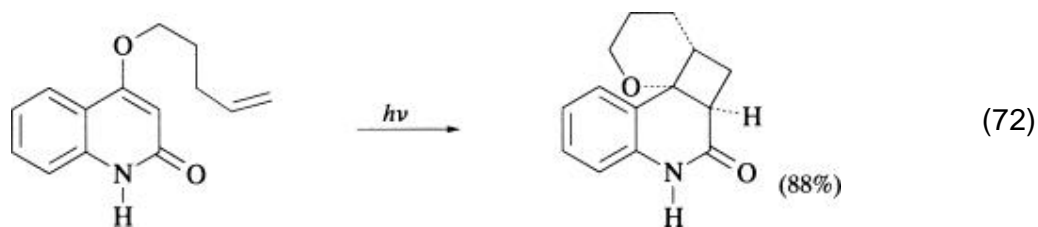
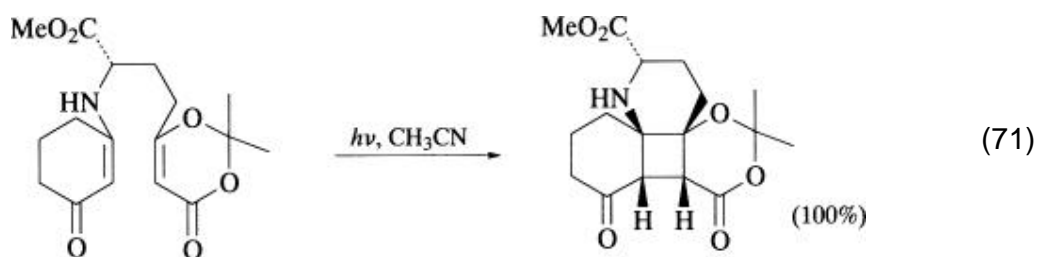
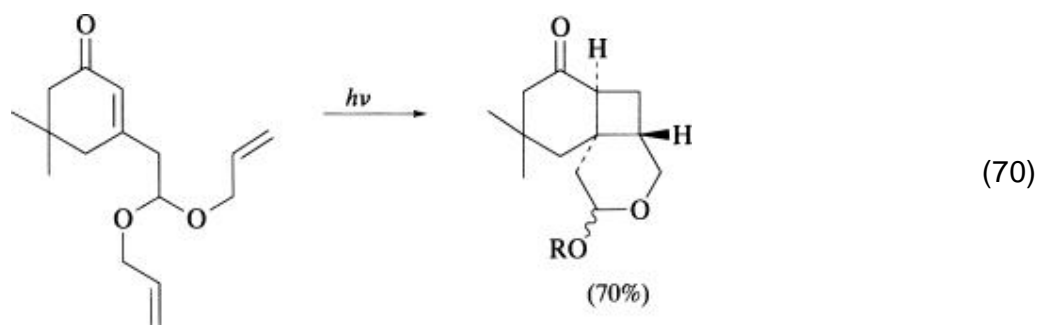
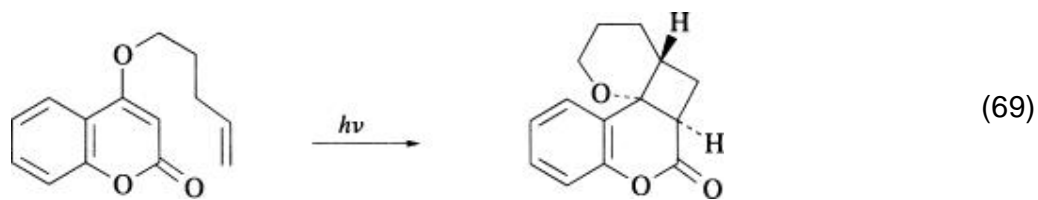
would be predicted in the *intermolecular* case. (113) Thus, the *intramolecular* nature of the reaction completely overrides the normal electronic preference observed in the intermolecular reaction (Eq. 66).



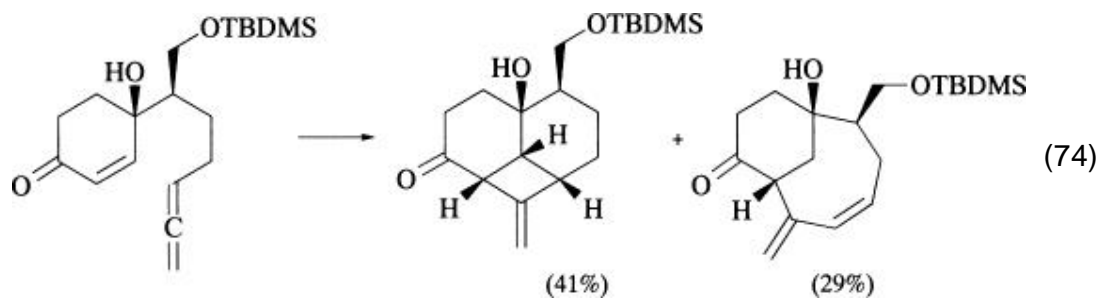
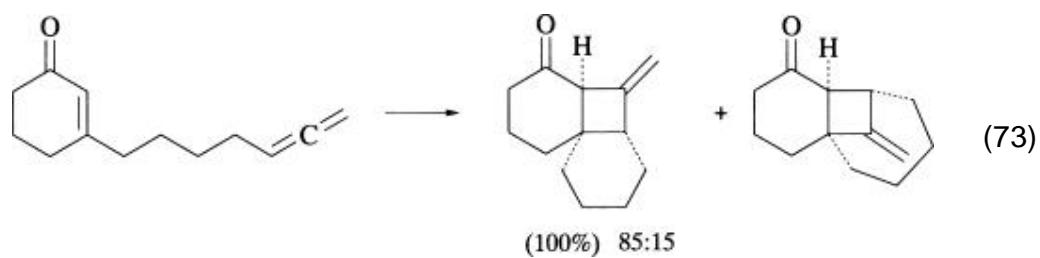


Enone-alkenes tethered by four atoms produce six-membered ring (straight) adducts regardless of the specific atoms in the tether (Eqs. 67–72). (114-119)
 The few exceptions to this observation usually involve allenes as the ground state alkene

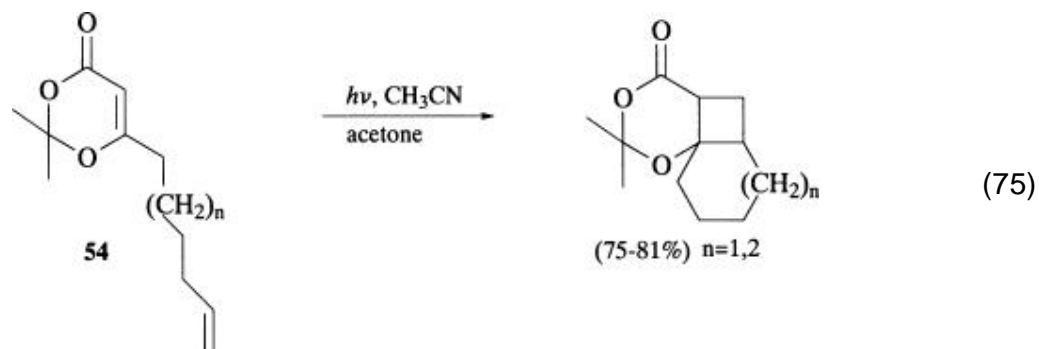


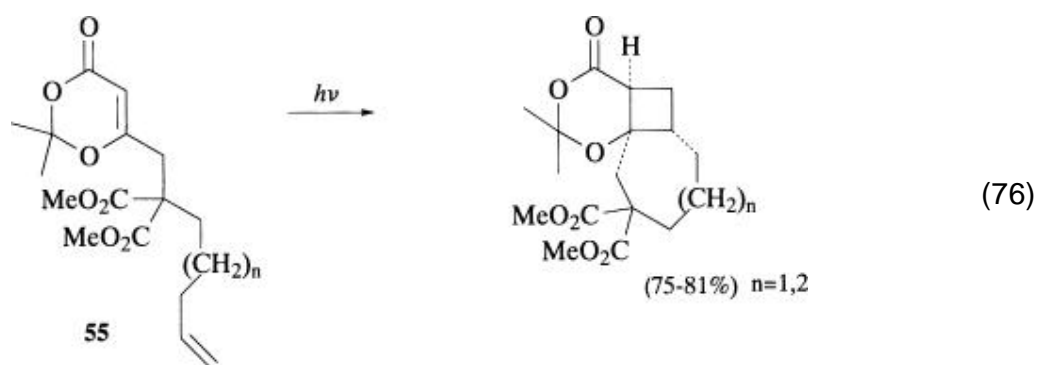


(Eqs. 73–74). (88, 120) These exceptions may reflect a different mechanistic pathway for photocycloadditions of enones and allenes. Despite the fact that the reaction of Eq. 68 is successful, esters are typically poor linkers because of unfavorable conformational preferences.



When the tether between the enone and alkene is more than four atoms, the straight adduct usually predominates. Dioxolenones [54–56](#) (Eqs. [75–76](#), [79](#)) ([121](#)) give the straight adducts exclusively, although dioxolenones are highly regioselective even in intermolecular photocycloaddition.

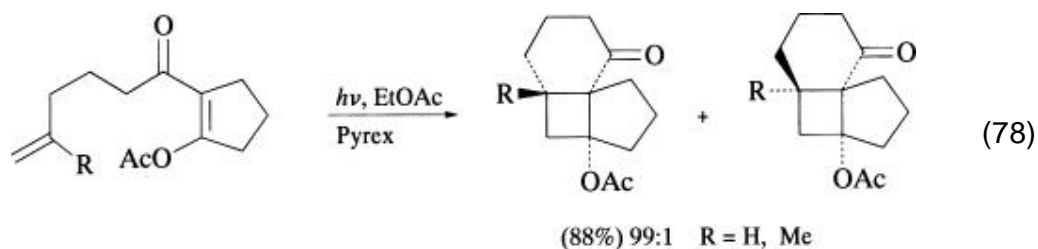
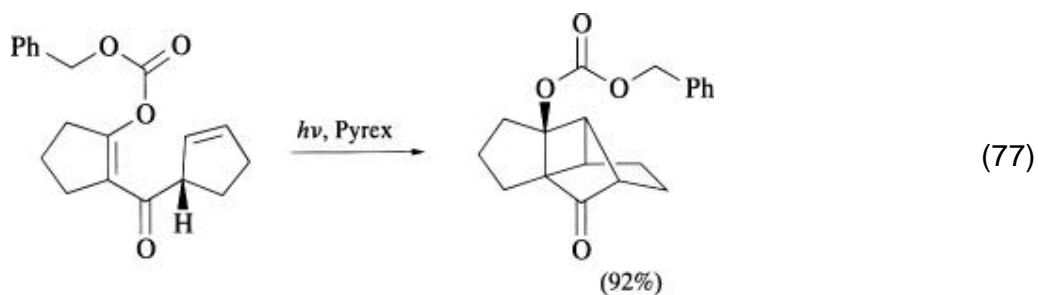


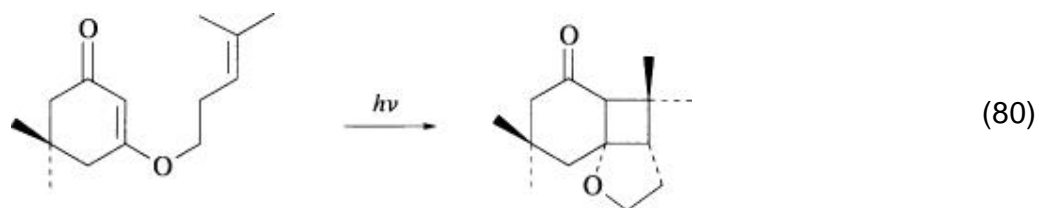
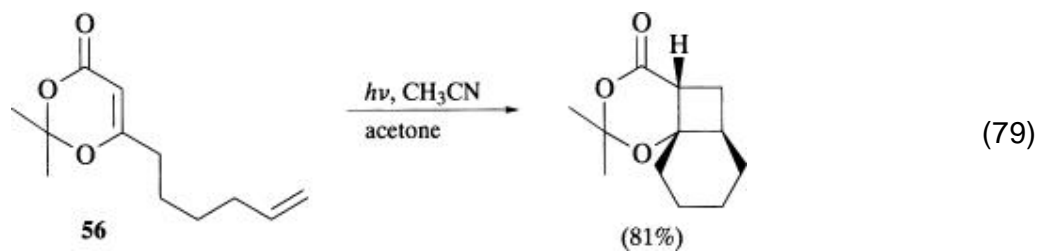


3.2.1.2. Stereoselectivity

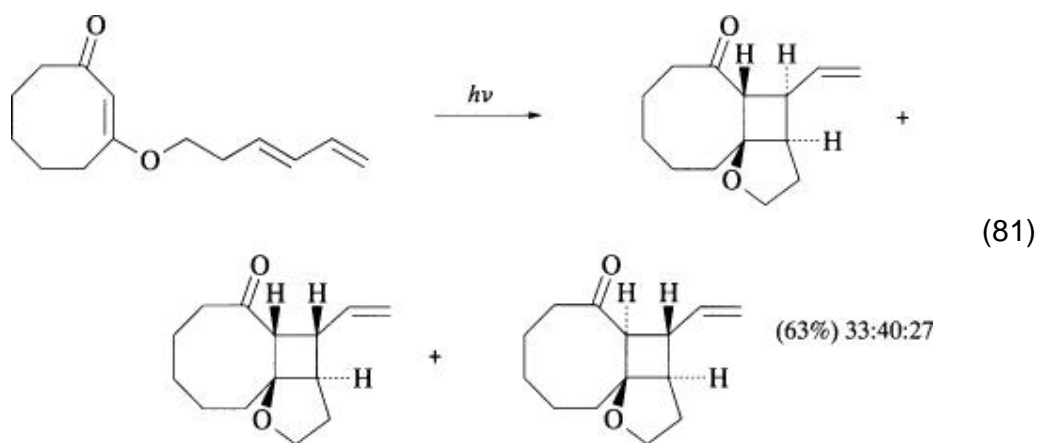
Intramolecular photocycloadditions are generally highly stereoselective. Additionally, stereogenic centers in the starting enone-alkene can be utilized to dictate the stereogenicity of newly formed stereocenters in the photoadduct. The preexisting stereogenic center can reside on the enone ring, on the tethering chain, or on a ring containing the ground state alkene.

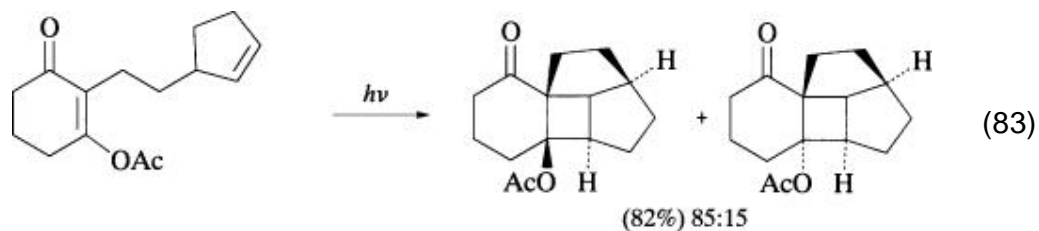
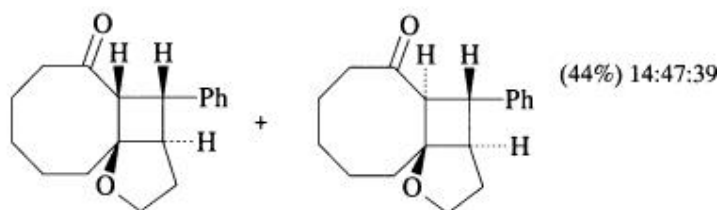
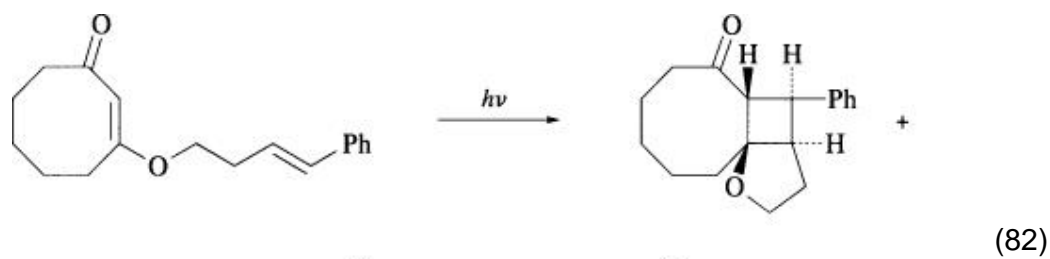
The stereochemistry of ring fusion between the cyclobutane and other rings in the photoadducts is almost always *cis* (Eqs. 77–80). (121-125) Exceptions can be found, but these usually result when the enone ring contains seven or more atoms, or



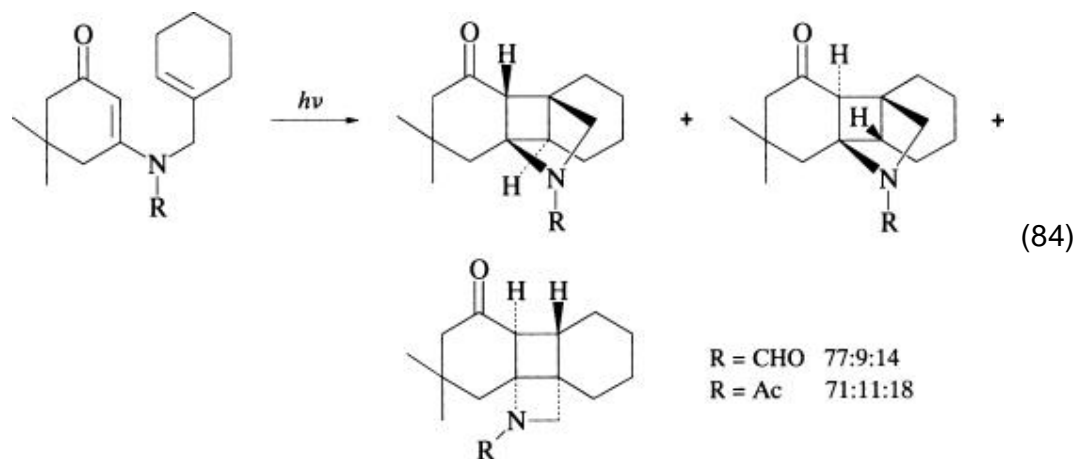


when the enone-alkene tether can easily accommodate the *trans* cyclobutane (Eqs. 81–84). (126-130) The most noteworthy exception is dioxolenone **57** which produces exclusively the *trans* 6–4 ring juncture in cycloadduct **58** (Eq. 85). This



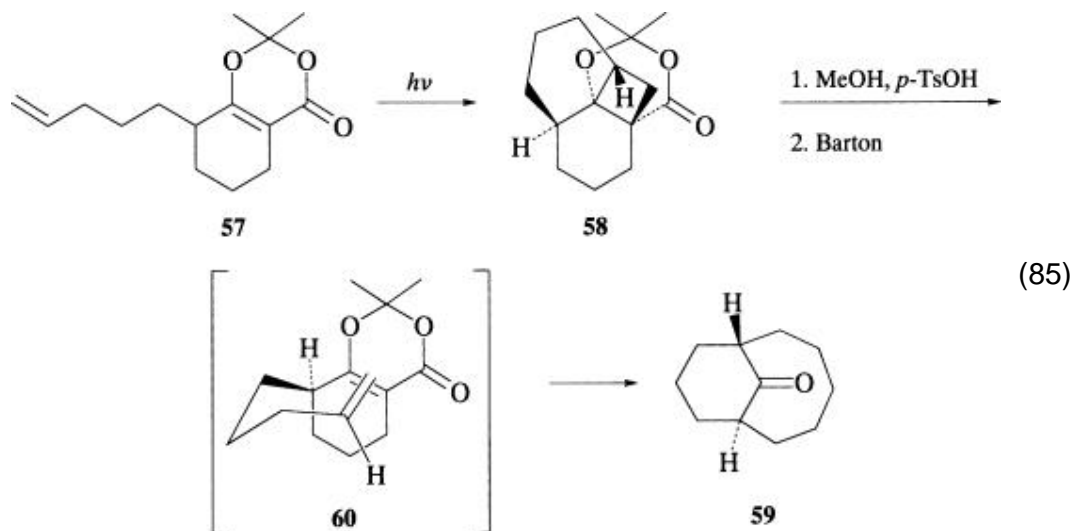


(82%) 85:15

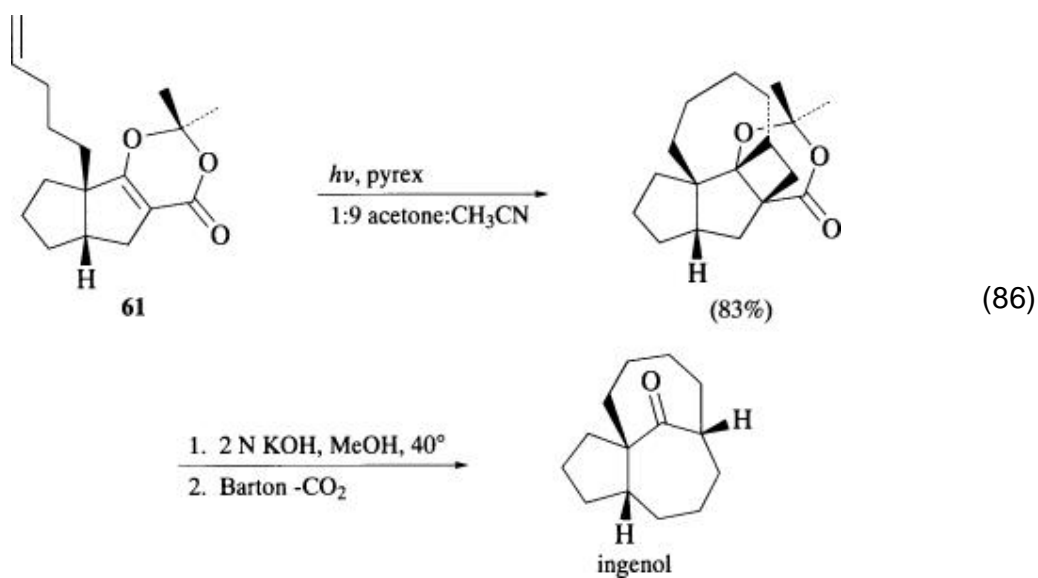


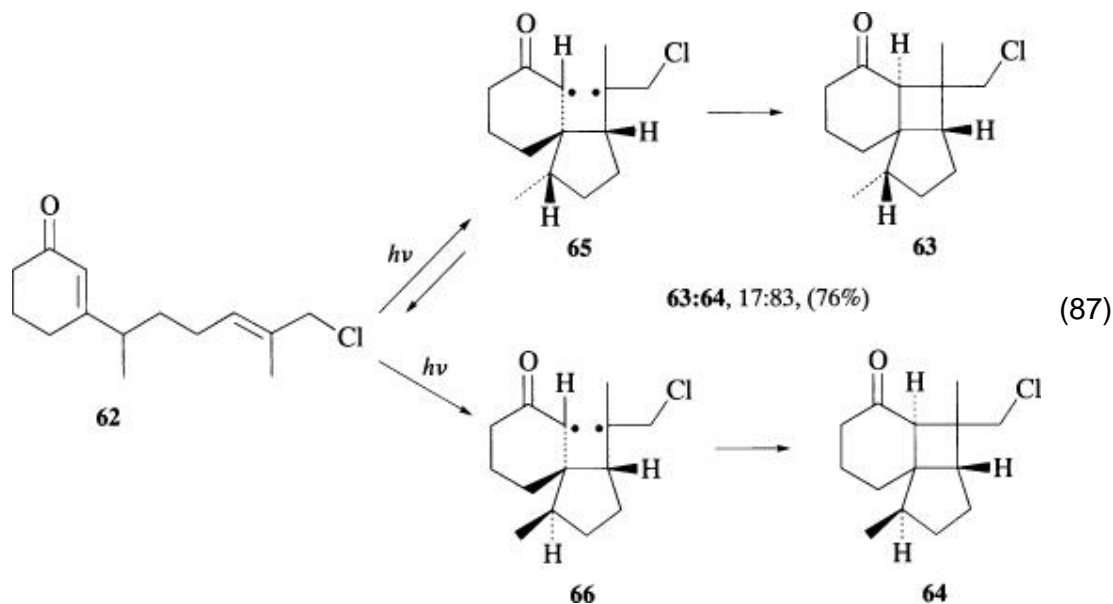
R = CHO 77:9:14
R = Ac 71:11:18

photoadduct can be converted to the smallest known inside-outside bicycloalkanone **59**. (131) The *trans* ring fusion presumably arises from initial bond formation through the chair-like conformation **60** (Eq. 85). Enone **61** is analogously transformed into the carbon skeleton of the naturally occurring inside-outside bicyclic compound ingenol (Eq. 86). (132)

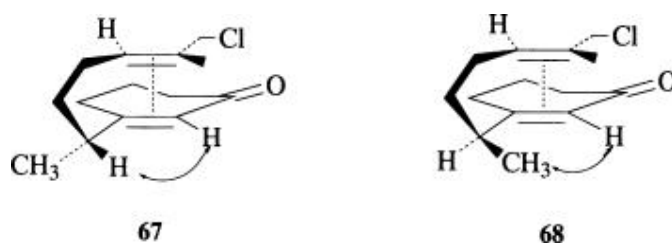


A stereogenic center on the tethering chain has been used to control the stereochemistry of a variety of polycyclic systems. Irradiation of cyclohexenone **62** produces a 1:5 mixture of the β : α methyl diastereomers **63:64** in 76% yield (Eq. 87). (133) A small amount of partially isomerized **62** is also isolated. The stereoselectivity can be rationalized in two ways. In one explanation product development control can be invoked. The rate of partitioning of the intermediate diradicals between products and ground state enone-alkene is different for the two



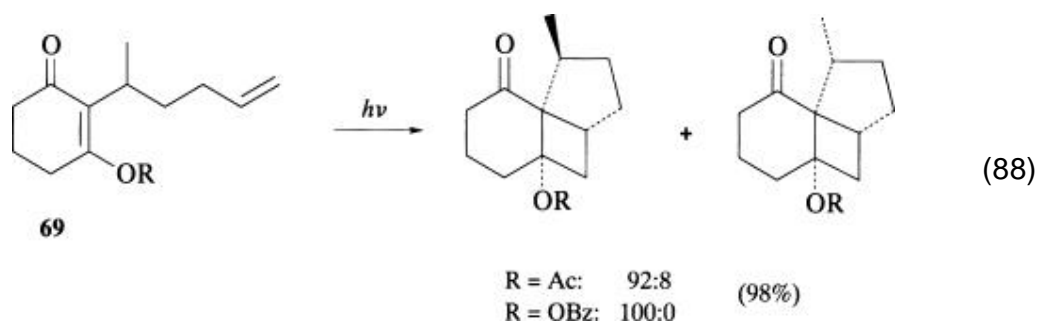


diradicals. Diradical **65** leading to the minor product would proceed slowly to cyclobutane **63** because of steric interaction between the secondary methyl group and the carbonyl α hydrogen during the final cyclobutane closure. Radical reversion to the starting enone alkene would predominate in this case. In diradical **66**, the steric interaction is absent as the diradical proceeds to the product. The resulting product ratio is presumed, therefore, to be a result of thermodynamic preference for the major product. Another rationale is that cycloadduct **64** predominates because of a kinetic preference for formation of the 1,4-diradical **66**, since the energy of exciplex **67** is lower than the energy of exciplex **68**. The $A_{1,3}$ interaction between the secondary methyl and the α -vinyl hydrogen raises the energy of exciplex **68** relative to exciplex

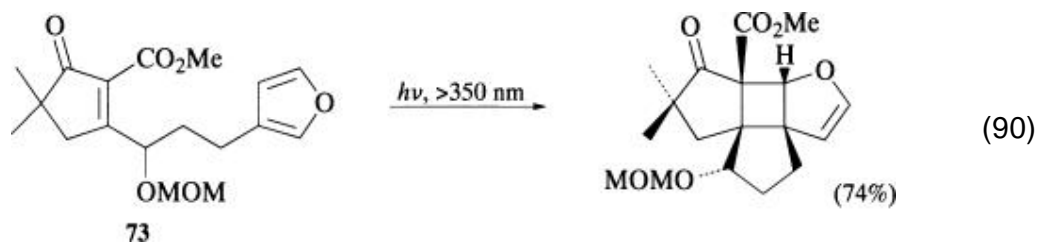
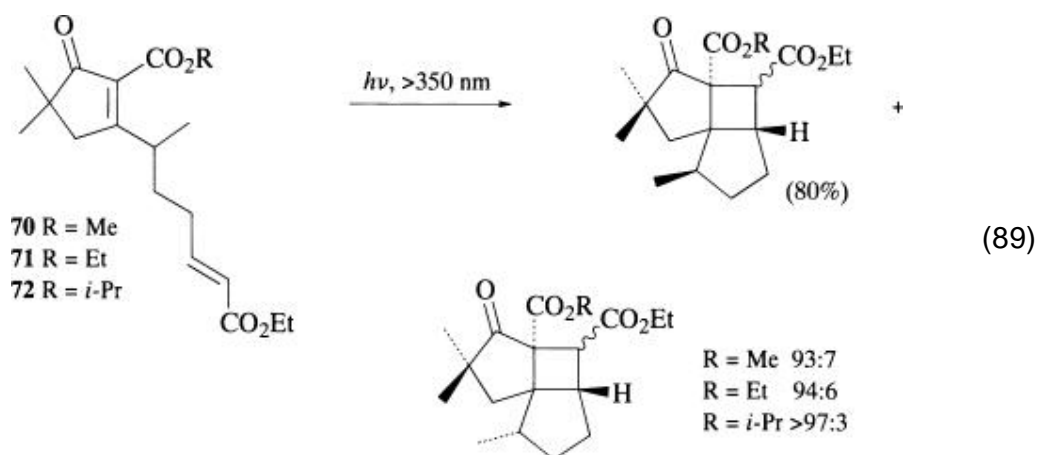


67, which has an $A_{1,3}$ interaction between two hydrogens. In some closely related systems there is no evidence of radical reversion. (134)

Regardless of which path is operative, the size of the vinyl substituent on the cycloalkenone clearly plays an important role in selectivity. Irradiation of enol acetate **69** gives a 92:8 mixture of diastereomers (Eq. 88), (135) whereas the corresponding

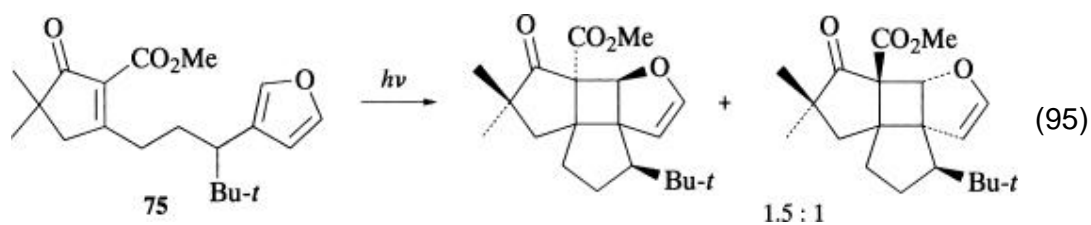
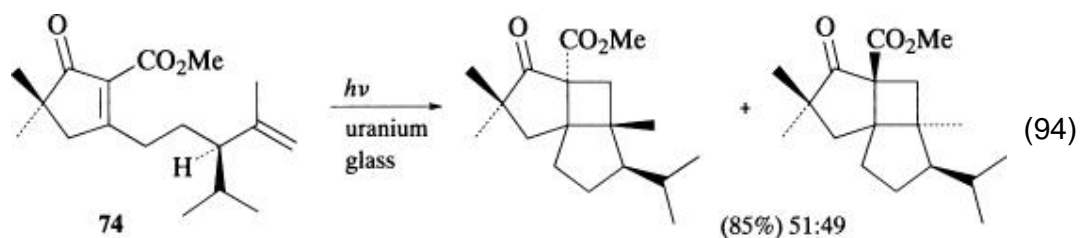
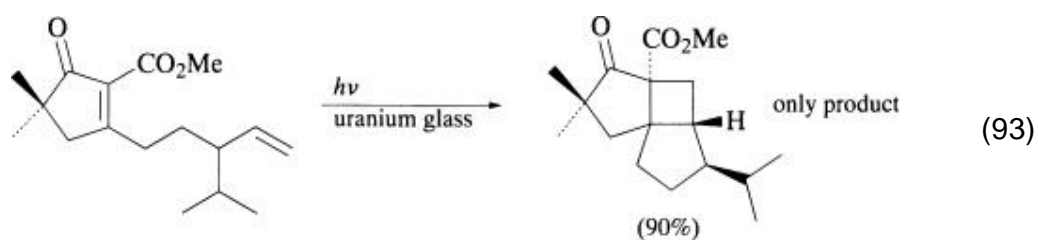
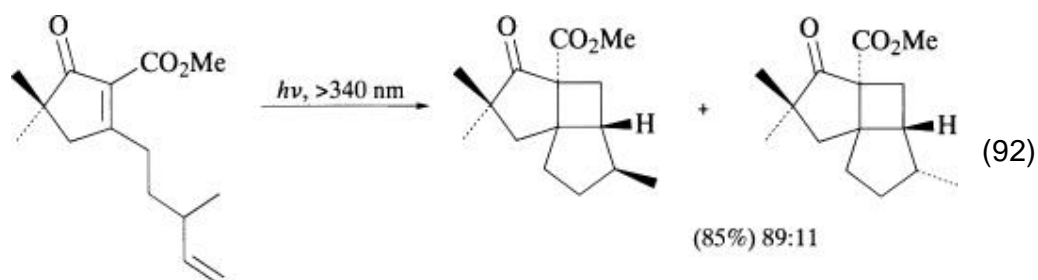
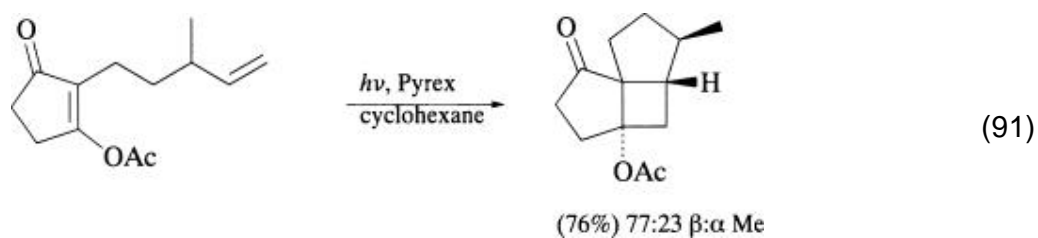


enol benzoate produces a single diastereomer presumably because of the increased steric interaction between the methyl group and the vinyl substituent. Similarly, a sequential increase in stereoselectivity is observed in the photocycloaddition of esters **70–72** from 93:7 with the methyl ester to >97:3 with the isopropyl ester (Eq. 89). (136, 137) Finally, enone **73** gives a single cycloadduct in high yield (Eq. 90). (138)



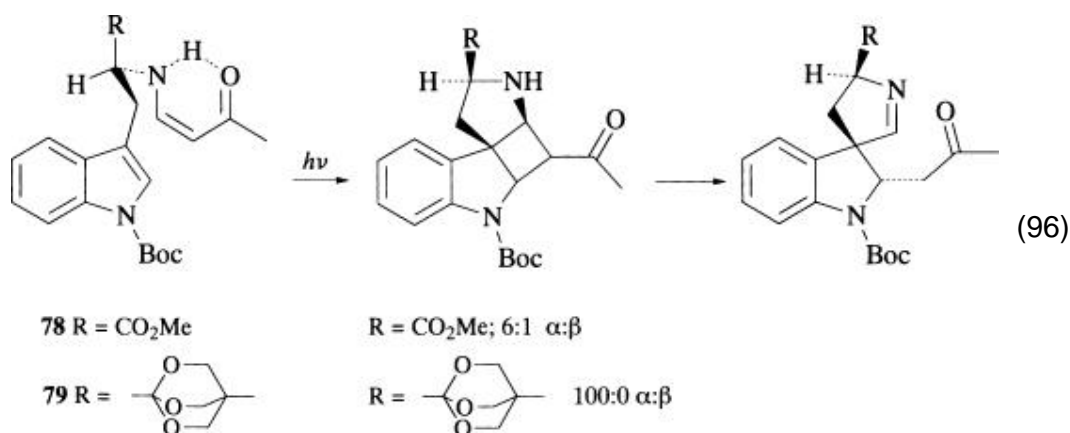
Good stereoselectivity is also observed when a stereogenic center is present at the other allylic position (Eqs. 91–93). (139–141) In contrast, when the internal carbon of the ground state alkene is substituted, the selectivity drops off dramatically as shown in the photoadditions of cyclopentenones **74** (141)

and **75**. (142) Apparently the $A_{1,2}$ strain between the vinyl substituent and the allylic substituent in exciplex **76** counterbalances the $A_{1,3}$ strain between the hydrogen and allylic substituent in exciplex **77** (Eqs. 94–95).

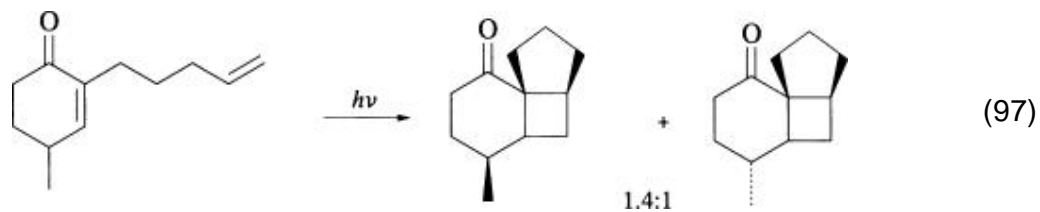




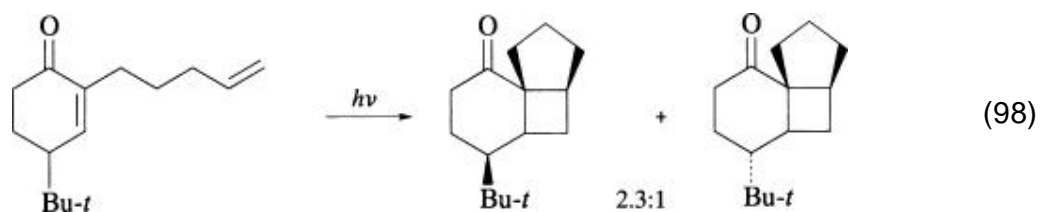
Good asymmetric induction is seen in the cycloaddition of enamide **78**. Even better selectivity is obtained when the methyl ester is converted to the ortho ester in enone **79** (Eq. 96). (118, 143, 144) The major product from **78** arises from an exciplex in a chair-like conformation with the methyl ester in an equatorial position. The minor isomer would require the substituent to occupy an axial site which would destabilize the transition state for the initial cyclization.



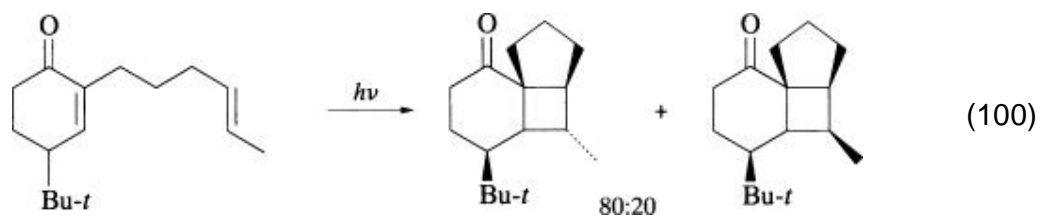
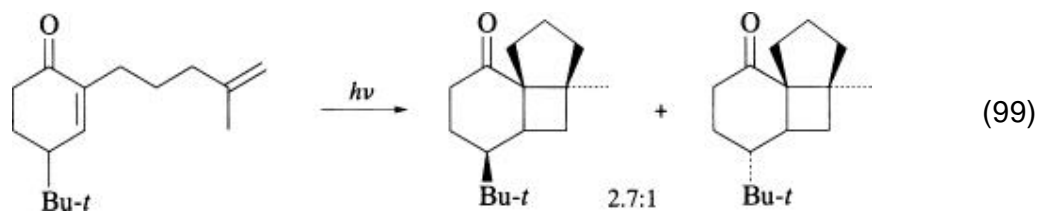
Modest levels of stereoselection can be achieved by incorporation of a preexisting stereogenic center at the 4 position of cyclohexenones with the tethering chain attached at the 2 position. (145) The substituent at the 4 position generally influences the olefin to approach the enone from the opposite face (Eq. 97); increasing the

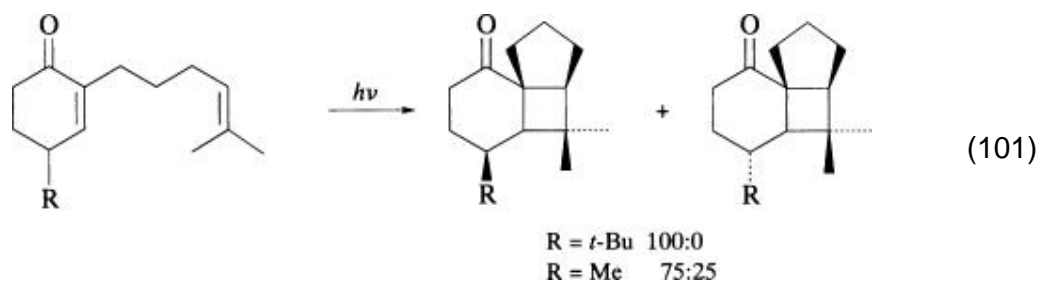


steric bulk of the C4 substituent results in a modest increase in stereoselectivity (Eq. 98). Substitution on the ground state alkene as well as the enone 4 position also

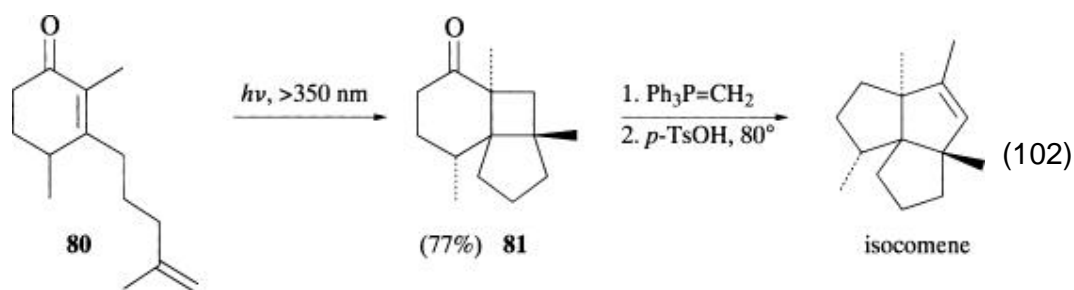


increases the selectivity, particularly when the substitution is on the terminus of the alkene in close proximity to the enone substituent (Eqs. 99–101). Similarly, enone

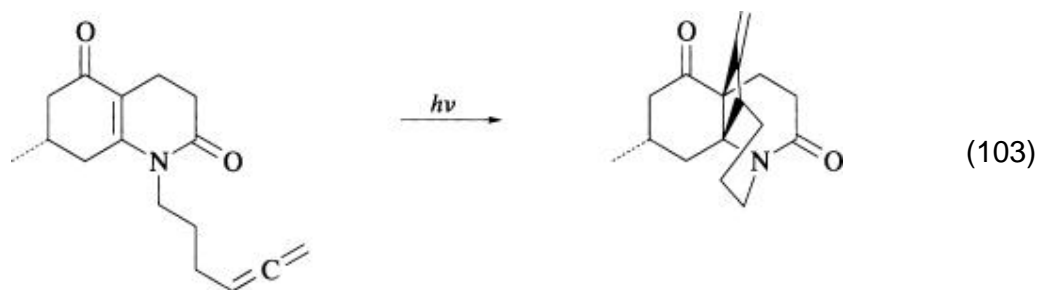


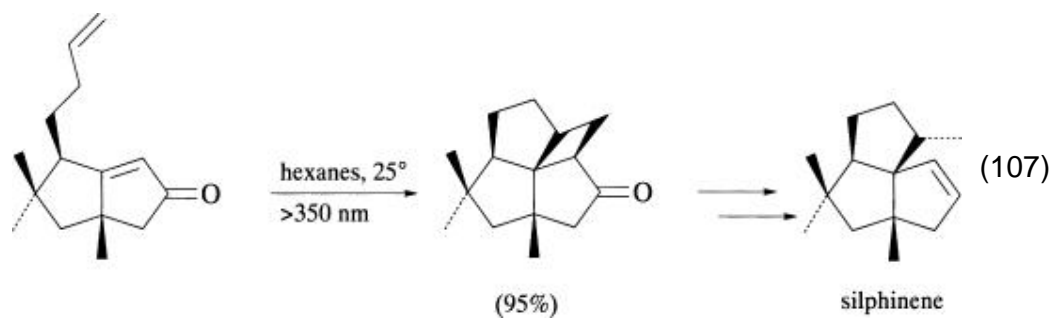
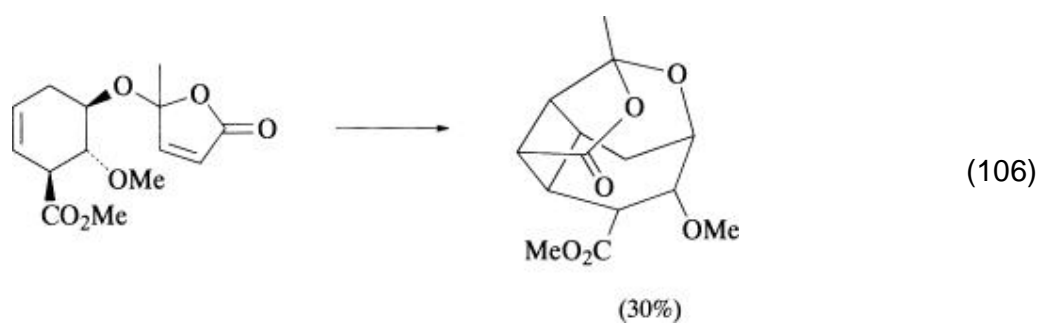
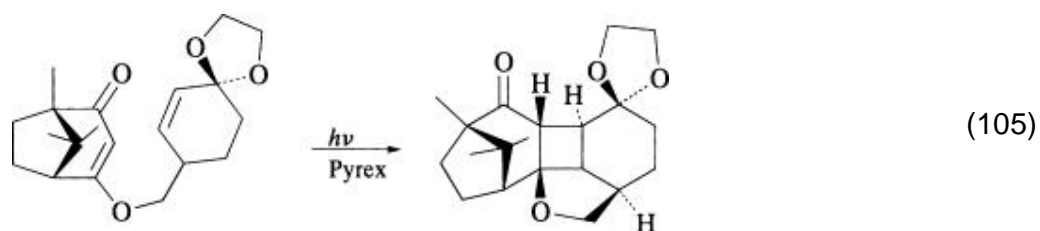
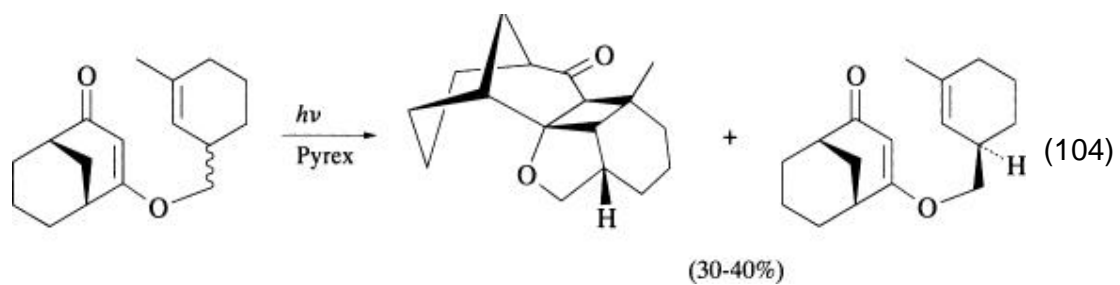


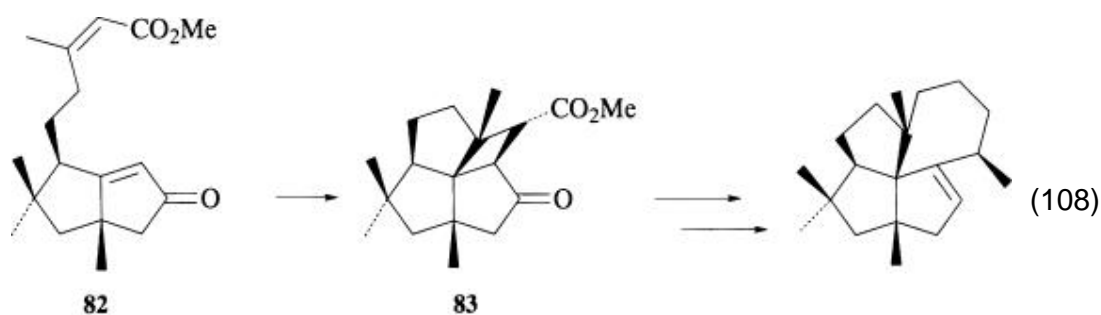
80 produces a single cycloadduct **81**, which can be readily converted to isocomene (Eq. 102). (146)



Some other interesting examples of stereocontrol in intramolecular photocycloadditions are shown in Eqs. 103–110. (72, 73, 140, 147-152) One striking example is diquinane enone **82**, which does not react when irradiated in hexanes at 25°, but undergoes rapid cycloaddition to **83** when irradiated at 110° in chlorobenzene at

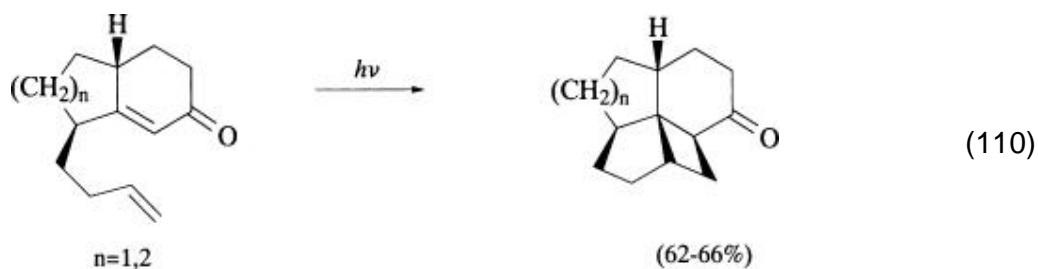
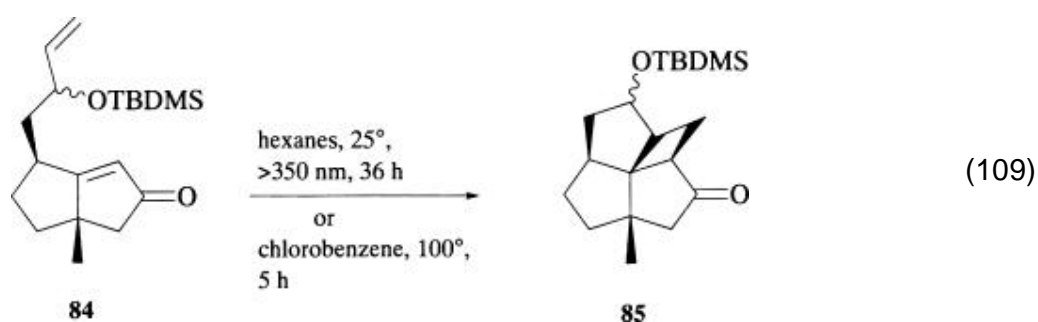






$h\nu$, 25°, hexanes: no reaction

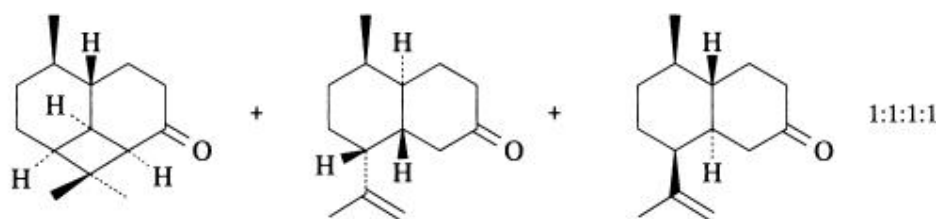
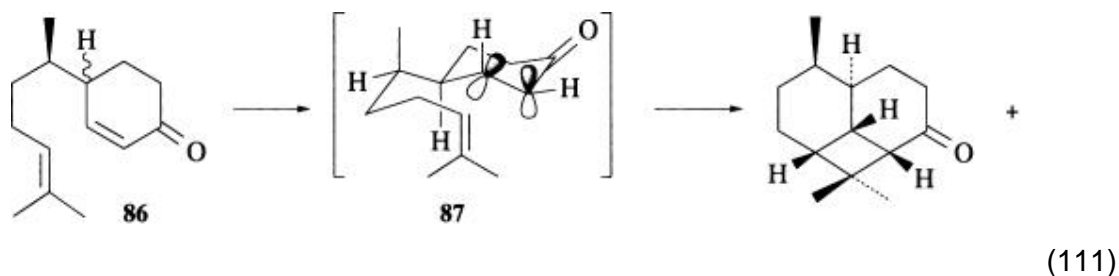
$h\nu$, C₆H₅Cl, 110° >350 nm: (87%), $\alpha:\beta$ CO₂Me = 1.5:1



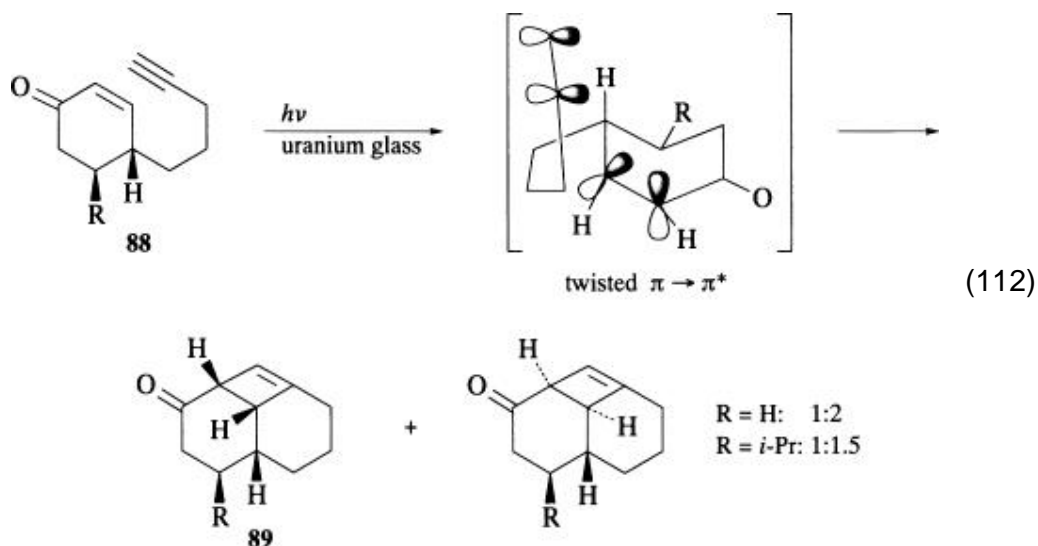
350 nm. (149, 151) In this system there is a severe nonbonded interaction between the angular and vinyl methyls in the transition state for initial cyclization. The success of the higher temperature reaction is probably a result of accessing the reactive conformation by overcoming this steric interaction. Similarly, enone **84** reacts slowly at room temperature and much more rapidly in chlorobenzene at 110°. (140) It is likely that other photocycloadditions which are sluggish at room temperature could benefit from higher temperature.

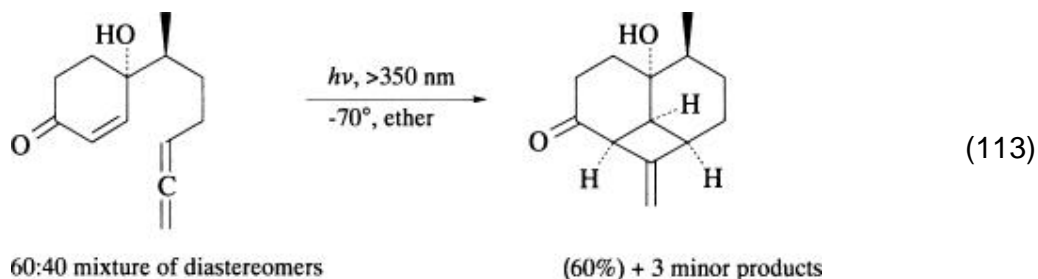
Cyclohexenones with the tether attached at the 4 position have not been as widely investigated as the 2- and 3-substituted cycloalkenones. A few important examples are known. The diastereomeric enones **86** give two cycloaddition products and two products from hydrogen atom abstraction, all

with *trans* ring junctures, upon cycloaddition (153) (Eq. 111). This result can be rationalized by assuming that the



excited triplet enone is twisted with the tether occupying a pseudo-equatorial site on the cycloalkenone as in 87. Predominantly *trans* products (154, 155) are obtained in the cycloaddition of 88 (Eq. 112). The *cis*-decalin 89 results because of the reduced degrees of freedom in the acetylene causing destabilization of the transition state for the initial formation of the *trans*-decalin. A variety of examples with allenes attached to cyclohexenones and cyclopentenones at the 4 position are also known. (88, 156-158)





3.3. Competing Reactions

One limitation of photocycloaddition reactions is that the excited state enone, the diradical intermediates, or the cyclobutane products can undergo competing reactions, which can complicate or even prevent normal photocycloaddition. In many cases these processes are absent or minimal; in many other cases they can be minimized by proper choice of reaction conditions.

As noted earlier, a limitation in the enone partner is that the double bond must be contained in a ring of six atoms or less to prevent energy-wasting *cis-trans* isomerization. This problem is not so important in the intramolecular reaction since the excited state is trapped much more efficiently because of the proximity of the alkene.

The excited enone can also undergo photocycloaddition with itself to produce dimers. This is only a problem in intermolecular reactions and can be reduced by increasing the amount of alkene or by sequential addition of small amounts of the enone. While it is not a common problem, enone excited states can produce oxetanes with the alkene or another enone, a photochemical process called the Paterno Buchi reaction.

The intermediate diradicals can undergo hydrogen atom abstraction to give products where only a single carbon-carbon bond has been formed. This is most often observed when the diradical has α, α -dimethyl substitution as in Eq. 90 or when the cyclobutane photoadduct would be highly strained. Solvent polarity can minimize this side reaction to some extent.

The most significant side reaction which can arise after cycloaddition is absorption of another photon by the carbonyl or some other chromophore in the molecule resulting in second-order cleavage reactions. This can almost always be prevented by utilizing light of longer wavelength to prevent absorption by the product cyclobutane.

Other competing reactions such as the photochemical di- π -methane

rearrangements, electrocyclic reactions, addition reactions, positional isomerization, photoenolization, and others can occur, but are rare, and do not warrant discussion here. ([159](#))

4. Experimental Conditions

A number of parameters can be important in experimentally executing a [2 + 2] photochemical cycloaddition. Choice of solvent, temperature, concentration, wavelength of light, and apparatus can be important.

4.1. Solvent

Any number of solvents can be utilized as long as the reactants are soluble. Some reactions, as noted in the text, are solvent dependent. Otherwise, hexanes, cyclohexane, acetone, acetonitrile, ether, dichloromethane, benzene, chlorobenzene, methanol, tetrahydrofuran, and many others are suitable. Mixtures of acetone and acetonitrile are particularly useful for certain enones such as dioxolenones since acetone serves as a triplet sensitizer. It is most often important to deoxygenate the solvent to help minimize radical side reactions. Also, for intermolecular reactions, olefin-free hexane can be advantageous, especially for small-scale reactions. Removal of olefins can be accomplished by stirring hexanes over concentrated sulfuric acid overnight, followed by washing with saturated sodium bicarbonate, drying, and distillation.

4.2. Temperature

In most cases temperature would not seem to be important, although reactions involving acyclic β -dicarbonyls as enones benefit from low temperatures to minimize *cis-trans* isomerization. Some reactions proceed slowly or not at all at room temperature and must be heated to effect reaction. Additionally the regiochemistry of some reactions is temperature dependent.

4.3. Concentration

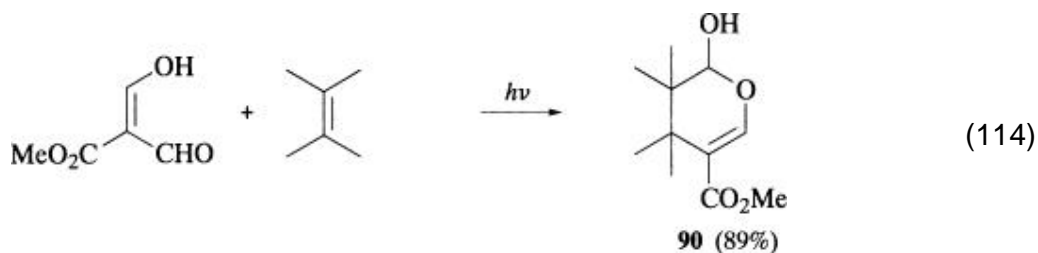
Intermolecular reactions proceed more rapidly at higher concentrations and it is often important to employ an excess (three to four equivalents) of the alkene to minimize dimerization of the enone as well as to maximize product yield. This can be a problem for alkenes which are expensive or must be prepared synthetically. The alkene can be recovered and recycled, or the enone can be added in small quantities until a nearly equimolar amount has been added. The intramolecular reaction is fairly independent of concentration, and high dilution techniques are not generally necessary unless a long tether is utilized.

4.4. Wavelength of Light

The wavelength of light used to carry out a photochemical cycloaddition reaction can often have a significant impact on the result. Wavelength can influence the rate of reaction by affecting the number of molecules which are in the excited state. The most severe adverse effect is probably the absorption of a photon by the initial cycloadduct leading to byproducts. If the proper wavelength is chosen, this can usually be avoided or at least minimized.

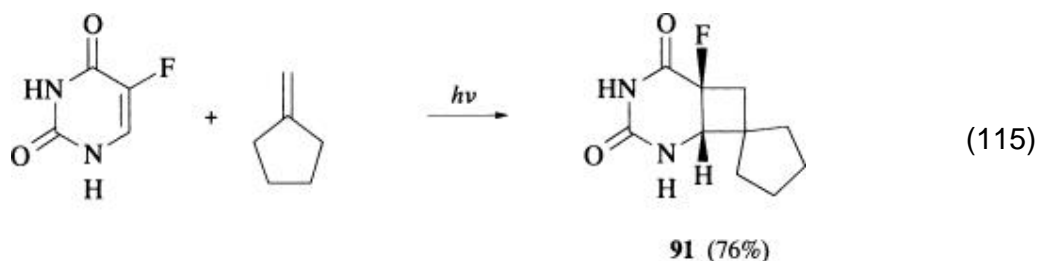
For preparative reactions the most common way to control wavelength is to utilize glass filters. Vycor glass allows light of $>220\text{--}230\text{ nm}$ to pass, while Pyrex is transparent to light $>290\text{--}300\text{ nm}$. For $>330\text{ nm}$ light a uranium glass filter can be used. Various combinations of filters available from Corning Glass can be used to isolate specific wavelengths; combinations of salt solutions and glass filters are also useful. A complete discussion of filters and solutions, as well as apparatus can be found in two previous reviews. ([160](#), [161](#))

5. Experimental Procedures



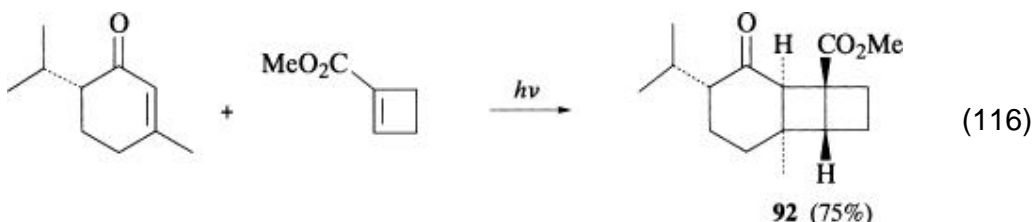
5.1.1.1. 4,4,5,5-Tetramethyl-6-hydroxy-5,6-dihydro-4H-pyran-3-carboxylic Acid Methyl Ester (**90**) (162)

In a 250-mL flame-dried Pyrex photochemical reactor equipped with a Claisen adapter, a water condenser, a fritted sintered glass gas inlet, and a jacketed (cooled by a water–methanol mixture) photochemical immersion well containing a 450-W Hanovia mercury lamp was placed a solution (796 mg, 6.12 mmol) of freshly distilled methyl diformylacetate and 2,3-dimethyl-2-butene (9.2 g, 109.5 mmol) in 3:1 pentane:dichloromethane. The solution was degassed for 30 minutes with nitrogen. The reactor was then immersed in a methanol–water–dry ice slurry and the solution was irradiated at -30 to -40° for 7 hours. Note: care must be taken to avoid freezing of water in the cooling jacket of the lamp. Removal of the solvent gave 1.170 g (89%) of essentially pure hemiacetal **90** as a viscous oil which crystallized on standing. Chromatography on silica gel followed by two recrystallizations from petroleum ether provided white prisms, mp 85 – 86° . $^1\text{H NMR}$ (CCl_4) δ 0.87 (3H, s), 0.93 (3H, s), 1.21 (6H, s), 3.62 (3H, s), 5.01 (1H, s), 5.25 (1H, s), 7.27 (1H, s); IR (KBr) 3440, 1680, 1620, 1280 cm^{-1} . Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{O}_4$: C, 61.66; H, 8.47. Found: C, 61.76; H, 8.59.



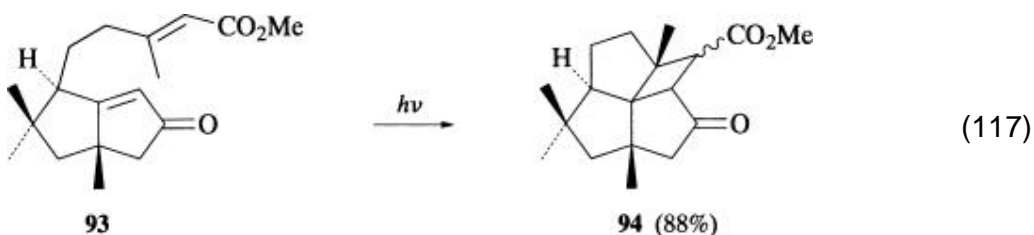
5.1.1.2. 6*ϕ*-Fluoro-*cis*-spiro[cyclopentane-1,8*ϕ*-[2,4]diazabicyclo[4.2.0]octane]-3*ϕ*,5*ϕ*-dione (**91**) (163)

A solution of 5-fluorouracil (0.39 g, 3 mmol) and 4 mL of methylenecyclopentane in 150 mL of acetone was placed in a standard photochemical reactor equipped with an immersion well, Corex filter sleeve, and a 450-W Hanovia mercury lamp. The solution was irradiated for 2 hours and the solvent was removed. The residue was recrystallized from ethyl acetate to give 0.47 g (76%) of photoadduct **91**, mp 265–266°. IR 1700 cm⁻¹. ¹H NMR (DMSO-*d*₆) δ 1.0–1.9 (8H, br m), 2.0–2.6 (m, partially obscured by DMSO), 3.95 (1H, d, *J* = 21 Hz), 8.02 (1H, s), 10.44 (1H, br s). Anal. Calcd for C₁₀H₁₃N₂O₂F : C, 56.6; H, 6.2; N, 13.2. Found: C, 56.7; H, 6.2; N, 13.2.



5.1.1.3. 2-Carbomethoxy-6-methyl-9-(1-methylethyl)tricyclo[4.4.0.0^{2,5}]decan-10-one (**92**) (164)

(-)-Piperitone [(4.38 g, 28.8 mmol), [α]_D 30.5° (c 0.334 g/mL), 61% ee] and methyl cyclobutanecarboxylate (3.23 g, 28.8 mmol) in 4.0 mL of dichloromethane were placed in a quartz test tube and the tube was sealed under argon with a septum. The mixture was cooled to -78° and irradiated by a 450-W Hanovia mercury lamp in a quartz immersion well until the vinyl proton of the ester had disappeared from the NMR spectrum. An additional 3.5 g (31.2 mmol) of the ester was added and the mixture was again irradiated until the vinyl proton of piperitone disappeared in the NMR. The solvent was removed and the crude product was chromatographed (4% ether in petroleum ether) to give 5.684 g (74.7%) of pure photoadduct **92**. Recrystallization from hexane gave about 40% recovery of optically pure product, mp 57–58°; IR (KBr) 1736, 1692 cm⁻¹; ¹H NMR δ 0.81 (3H, d, *J* = 7.6 Hz), 0.93 (3H, d, *J* = 7.6 Hz), 1.22 (3H, s), 2.90 (1H, s), 3.62 (3H, s). Anal. Calcd for C₁₆H₂₄O₃: C, 72.69; H, 9.15. Found: C, 72.94; H, 9.06.

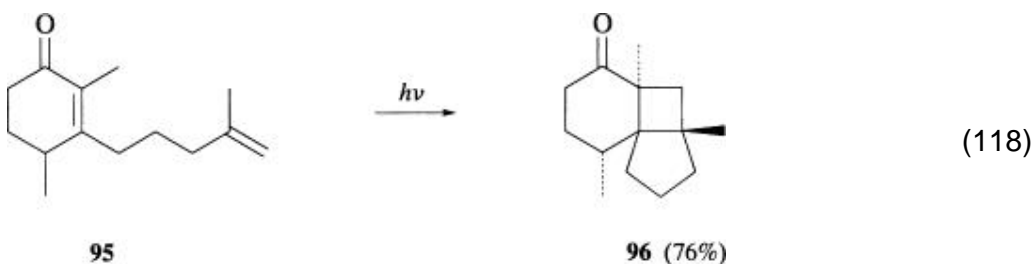


5.1.1.4. (1*SR*,4*RS*,7*SR*,9*SR*,12*RS*)-8-Carbomethoxy-2,2,4,10-tetramethyltetraacyclo [5.4.1.0^{4,12}]dodecan-6-one (**94**) (151)

A solution of 1.36 g (4.7 mmol) of enone **93** in 75 mL of chlorobenzene was placed in a toroidal Pyrex reactor inside which was placed a Pyrex immersion well containing a uranium glass filter sleeve and a 450-W medium pressure Hanovia mercury vapor lamp. The reactor was wrapped with heating tape and heated to 110°. The lamp was turned on and the solution was irradiated for 4.5 hours. The lamp was turned off and the solution was allowed to cool to room temperature. The chlorobenzene was removed under vacuum and the residual material was flash chromatographed (100 g silica gel, 1:9 ethyl acetate:hexanes) to give 714 mg (53%) of the α isomer as a colorless oil and 476 mg (35%) of the β isomer as a crystalline solid (m.p. 76–79°).

α Isomer **94a**: ¹H NMR (250 MHz, CDCl₃) δ 0.96 (s, 3H), 1.01 (s, 3H), 1.36 (s, 3H), 1.39 (s, 3H), 1.46–1.89 (band, 6H), 2.08–2.36 (band, 2H), 2.59 (dd, $J = 2, 15$ Hz, 1H), 2.79 (d, $J = 9$ Hz, 1H), 2.93 (d, $J = 10$ Hz, 1H), 3.7 (s, 3H). IR (CDCl₃) 2960, 1735, 1255, 1205 cm⁻¹. Anal. Calcd for C₁₈H₂₆O₃: C, 74.45; H, 9.02. Found: C, 74.10; H, 9.20.

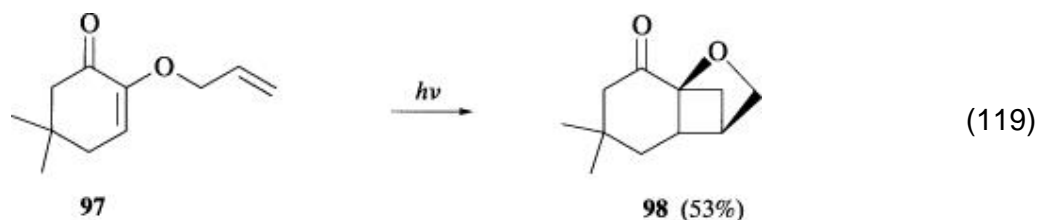
β Isomer **94b**: ¹H NMR (250 MHz, CDCl₃) δ 1.03 (s, 3H), 1.06 (s, 3H), 1.24 (s, 3H), 1.45 (s, 3H), 1.61–2.16 (band, 6H), 2.28 (dd, $J = 10, 15$ Hz, 1H), 2.43 (dd, $J = 2, 15$ Hz, 1H), 2.64 (m, 2H), 3.18 (d, $J = 12.5$ Hz, 1H), 3.64 (s, 3H). IR (CDCl₃) 2950, 1730, 1155 cm⁻¹. Anal. Calcd for C₁₈H₂₆O₃: C, 74.45; H, 9.02. Found: C, 74.17; H, 9.02.



5.1.1.5. 2 α , 6 α , 8 β -Trimethyltricyclo[6.3.0.0^{1,6}]undecan-5-one (**96**) (146)

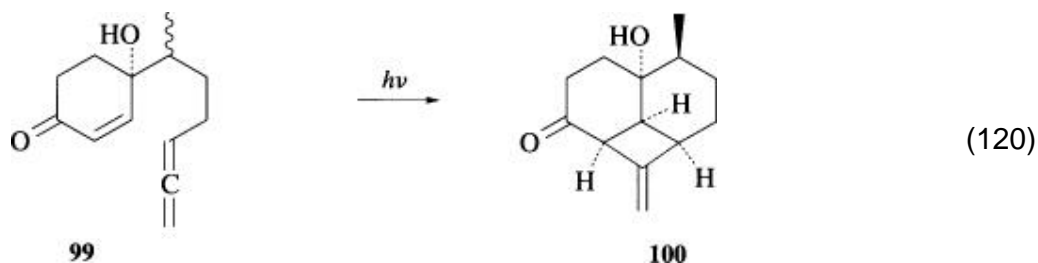
Nitrogen was bubbled through a solution of enone **95** (6.18 g, 30 mmol) in 3 L of LC grade hexane in a 3-L round-bottom flask for 30 minutes. The flask was sealed and placed in a Rayonet reactor fitted with 350-nm lamps. The solution was irradiated for 24 hours and the solvent was removed in vacuo. The residue was purified by preparative HPLC (1:9 ether:hexane) to give 4.72 g (76%) of cycloadduct **96**. Kugelrohr distillation (130°, 0.4 mm) gave a waxy solid, mp

63–68°. IR: 1705, 1460, 1450, 1440, 1380, 1275, 1180, 1080, 1060, 1040, 1020, 1000, 940 cm^{-1} . ^1H NMR: δ 0.83 (3H, d, $J = 12$ Hz), 1.00 (3H, s), 1.10 (3H, s), 1.33 (1H, d, $J = 12$ Hz), 2.30 (1H, d, $J = 12$ Hz). ^{13}C NMR: δ 18.1 (q), 19.4 (q), 22.2 (q), 24.8 (t), 26.7 (t), 28.9 (t), 33.3 (d), 36.7 (t), 41.0 (t), 44.5 (s), 46.4 (s), 56.5 (s), 217.7 (s).



5.1.1.6. (1*RS*,6*RS*,7*SR*)-4,4-Dimethyl-9-oxatricyclo[5.2.1.0^{1,6}]decan-2-one (**98**) (165)

A solution of enone **97** (730 mg, 4.1 mmol) in acetone (73 mL) was placed in a Pyrex tube and irradiated for 2 hours with an Eikosha 350-W high pressure mercury lamp which was contained in an immersion well equipped with a Pyrex filter sleeve. Evaporation of the solvent yielded 390 mg (53%) of cycloadduct **98**, mp 75.5–76°. IR (CCl₄) 1725 cm^{-1} ; ^1H NMR (CDCl₃) δ 0.90 (3H, s), 1.12 (3H, s), 1.7–2.6 (6H, band), 2.7–2.85 (1H, m), 2.82 (1H, s), 3.84, 3.93 (2H, AB, $J = 6$ Hz). Anal. Calcd for C₁₁H₁₆O₂: C, 73.30; H, 8.95. Found: C, 73.13; H, 9.09.



5.1.1.7. (1*S*^{*},2*R*^{*},5*S*^{*},7*R*^{*},11*R*^{*})-1-Hydroxy-2-methyl-6-methylenetricyclo[5.3.1.0^{5,11}]undecan-8-one (**100**) (156)

A solution of the diastereomeric enones **99** (900 mg, 4.37 mmol) in 650 mL of dry, distilled ether was placed in a Pyrex irradiation vessel (vacuum jacketed to allow water cooling for the lamp while the contents are at low temperature) and purged with nitrogen. The vessel was placed in an insulated cannister containing isopropyl alcohol which was maintained at –70° with a Cryocool. The solution was irradiated for 20 hours with a 450-W Hanovia lamp fitted with

a uranium glass filter. The solvent was evaporated and the oily product was purified by flash chromatography (15–30% ethyl acetate–hexane gradient) to give 520 mg of 75% pure cycloadduct **100** (capillary GC analysis). Spectral and analytical data were obtained on pure fractions of the product. IR (thin film) 3480, 3080, 1700 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.97 (3H, d, $J = 6.5$ Hz), 1.40–1.82 (7H, m), 2.05–2.65 (4H, m), 3.29–3.41 (1H, m), 3.64 (1H, d, $J = 8$ Hz), 4.73–4.76 (2H, m); ^{13}C NMR (CDCl_3) δ 14.4, 22.6, 24.6, 27.3, 33.8, 40.4, 42.6, 42.7, 53.2, 71.2, 101.9, 148.9, 209.3; exact mass calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: 206.1307. Found: 206.1311.

6. Tabular Survey

The contents of the tables were derived by searching *Chemical Abstracts* and *Science Citation Index*. An extensive computer search was conducted in *Chemical Abstracts* from 1967 through 1989. The literature prior to 1967 was searched by hand.

The tabular organization of the intermolecular reaction begins with all-carbon rings. Cyclopropenes are followed by cyclobutenes, cyclopentenones, cyclohexenones, and multicyclic enones. Within these individual tables the enones are organized by increasing *total* carbon number. If two enones have the same carbon they are sequenced by increasing total hydrogen number. For different alkenes with the same enone, the entries are sequenced by increasing *total* carbon number of the alkene. Following the all-carbon rings are oxygen-containing rings and then nitrogen-containing rings.

The intramolecular tables are organized beginning with cyclopentenones with an all-carbon alkene tether attached at the 2 position. These are followed by 3-, 4-, and 5-alkenyl cyclopentenones with all-carbon tethers. Order of entry is again determined by *total* carbon number and then total hydrogen number. Cyclopentenones with oxygen-containing tethers are then entered in the same substituent sequence. Cyclohexenones are then treated in a similar manner. These are followed by bridged bicyclic enone-alkenes, dioxolenones, butenolides, nitrogen-containing enones, lactones, lactams, and acyclic hexadienones.

Yields in parentheses are isolated yields; numbers separated by colons are ratios of products. A dash indicates that no data for yield or reaction conditions were given. The following abbreviations are used in the tables:

Ac	acetyl
Corex	Corex glass filter sleeve
Ether	diethyl ether
MEM	methoxyethoxymethyl
MOM	methoxymethyl
Pyrex	Pyrex glass filter sleeve
TBDMS	<i>tert</i> -butyldimethylsilyl
Tr	trityl (triphenylmethyl)
Vycor	Vycor glass filter sleeve
Uranium	uranium glass filter sleeve

Table I. Cyclopropene or Cyclobutene Carboxylates and Alkenes

[View PDF](#)

Table II. Cyclopentenone and Alkenes or Acetylenes

[View PDF](#)

Table III. Substituted Cyclopentenones and Alkenes or Acetylenes

[View PDF](#)

Table IV. Cyclohexenone and Alkenes or Acetylenes

[View PDF](#)

Table V. Substituted Cyclohexenones and Alkenes or Acetylenes

[View PDF](#)

Table VI. Polycyclic Cyclohexenones and Alkenes or Acetylenes

[View PDF](#)

Table VII. Benzoquinones and Alkenes

[View PDF](#)

Table VIII. Cyclohexadienes or Cyclohexenediones and Alkenes

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Table IX. Oxaenones and Alkenes

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Table X. Pyrimidines and Alkenes or Acetylenes

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Table XI. Azaenones and Alkenes or Acetylenes

[View PDF](#)

Table XII. Enols of β -Dicarbonyls and Alkenes

[View PDF](#)

Table XIII. 2-Alkenylcyclopentenones

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Table XIV. 3-Alkenylcyclopentenones

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Table XV. 4-Alkenylcyclopentenones

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Table XVI. 5-Alkenylcyclopentenones

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Table XVII. Diquinane Enones

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Table XVIII. Oxygen Tethered 2-Alkenylcyclopentenones

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Table XIX. Oxygen Tethered 3-Alkenylcyclopentenones

[View PDF](#)

Table XX. Oxygen Tethered 4-Alkenylcyclopentenones

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Table XXI. 2-Alkenylcyclohexenones

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Table XXII. 3-Alkenylcyclohexenones

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Table XXIII. 4-Alkenylcyclohexenones

[View PDF](#)

Table XXIV. 5-Alkenylcyclohexenones

[View PDF](#)

Table XXV. 6-Alkenylcyclohexenones

[View PDF](#)

Table XXVI. Nitrogen Tethered 2-Alkenylcyclohexenones

[View PDF](#)

Table XXVII. Nitrogen Tethered 3-Alkenylcyclohexenones

[View PDF](#)

Table XXVIII. Oxygen Tethered 2-Alkenylcyclohexenones

[View PDF](#)

Table XXIX. Oxygen Tethered 3-Alkenylcyclohexenones

[View PDF](#)

Table XXX. Oxygen Tethered 3-Alkenylcyclooctenones

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Table XXXI. Bridged Bicyclic Dienes

[View PDF](#)

Table XXXII. 3-Alkenyldioxolenones

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Table XXXIII. 4-Alkenylbutenolides

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Table XXXIV. Miscellaneous Nitrogen Containing Cyclic Enones

[View PDF](#)

Table XXXV. Alkenylpyrimidines

[View PDF](#)

Table XXXVI. Alkenylbenzopyranones

[View PDF](#)

Table XXXVII. Alkenylbenzolactams

[View PDF](#)

Table XXXVIII. 1,5-Hexadien-3-ones

[View PDF](#)

Table XXXIX. 1-Acyl-1,5-hexadienes

[View PDF](#)

Table XL. 2-Acyl-1,5-hexadienes

[View PDF](#)

Table XLI. 1,6-Heptadien-3-ones

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Table XLII. 3-Aza-1,5-hexadienes

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Table XLIII. Miscellaneous Oxygen Containing Enones

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TABLE I. CYCLOPROPENE OR CYCLOBUTENE CARBOXYLATES AND ALKENES

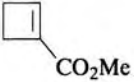
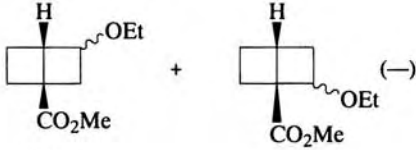

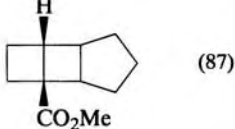
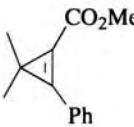
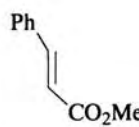
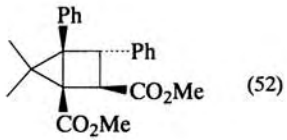
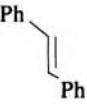
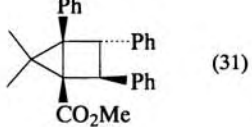
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	CH ₂ =CHOEt	Quartz, CH ₂ Cl ₂ , 0°, 3 h	 (—)	57
		—	 (87)	57, 58
C ₁₃ 		Uranium, C ₆ H ₆ , 30 h, thioxanthenone	 (52)	166
		Uranium, C ₆ H ₆ , 100 h, thioxanthenone	 (31)	166

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES

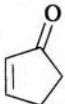
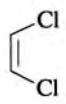
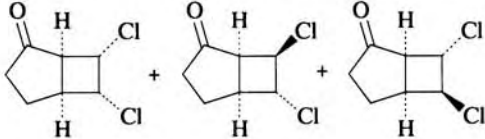
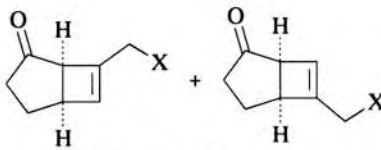
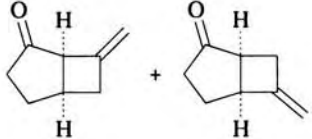
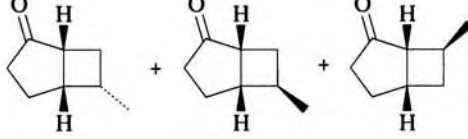
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	 <i>cis-</i> <i>trans-</i>	Pyrex, 20°	 29:19:52 (—) 48:30:22 (—)	167
	HC≡CCH ₂ X	Benzene, 48 h Benzene, 48 h Acetone, -78°, 2 h	 X = OH 69:20 (7) X = Cl 72:19 (29) X = H 20:80 (68)	168 168 169
	CH ₂ =C=CH ₂	Pyrex, benzene	 85:15 (62)	170
	CH ₂ =CH ₂	Uranium, 6 h	 9:34:57 (—)	169

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

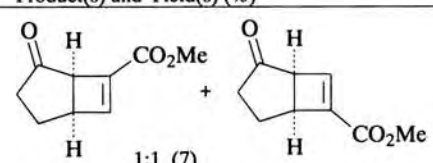
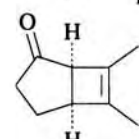
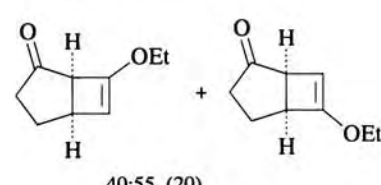
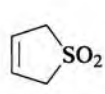
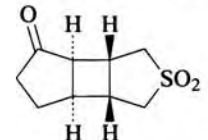
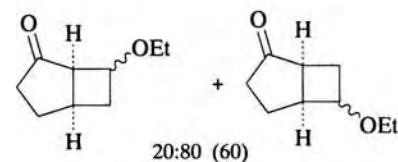
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{HC}\equiv\text{CCO}_2\text{Me}$	—	 1:1 (7)	168
	$\text{MeC}\equiv\text{CMe}$	Pyrex	 (60)	170
	$\text{HC}\equiv\text{COEt}$	>300 nm, benzene or ether	 40:55 (20)	168
		CH_2Cl_2 , quartz	 (25)	171
	$\text{CH}_2=\text{CHOEt}$	366 nm, pentane	 20:80 (60)	172

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

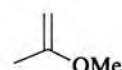
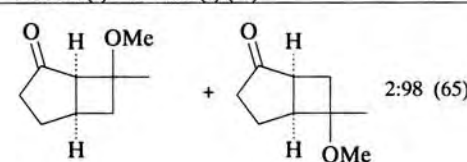
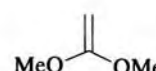
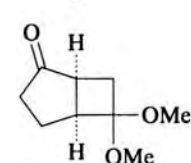

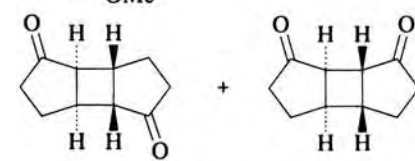

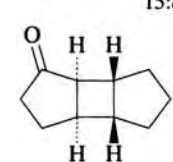
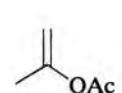
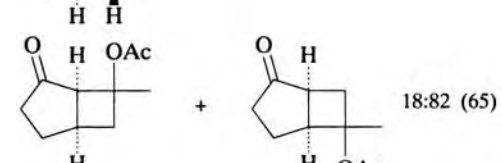
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, pentane	 2:98 (65)	172
		366 nm, pentane	 (60) (65)	28 172
		Pyrex, 24 h, neat Benzene, 0.1 M	 1:1 (—) 15:85 (—)	26,173 173,61
		Pyrex, 3 h	 (67)	27
		366 nm, pentane	 18:82 (65)	172

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

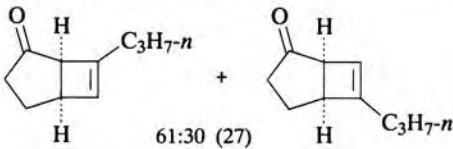
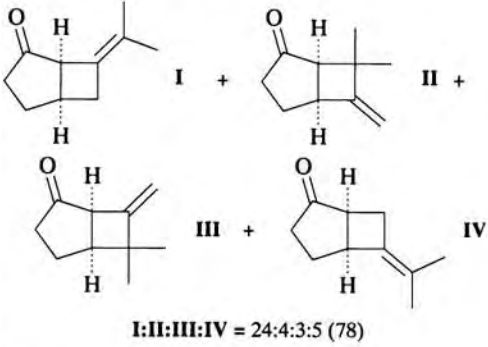
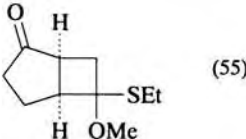
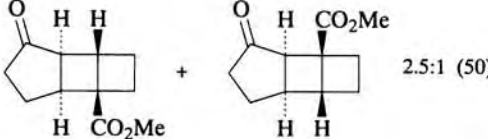
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{HC}\equiv\text{CC}_3\text{H}_7\text{-}n$	Benzene		168
	$\text{CH}_2=\text{C}=\text{C}(\text{Me})_2$	Pyrex, ethanol		174, 175
	$\text{MeO}-\text{C}(\text{Me})=\text{SEt}$	366 nm, pentane		172
	CO_2Me	—		58

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

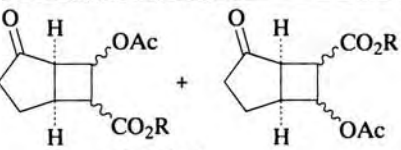
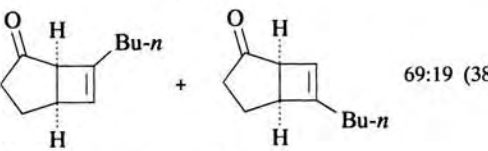
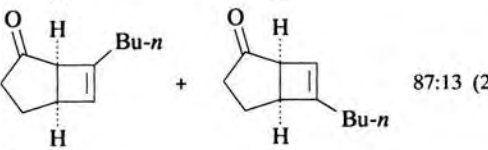
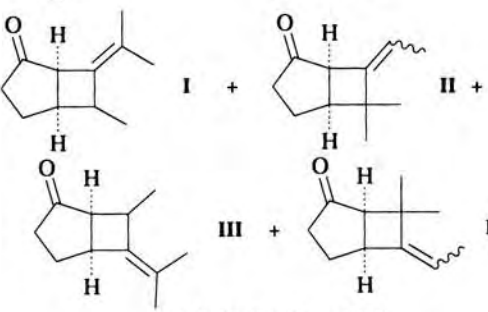
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CO_2R OAc	Benzene 366 nm, pentane, 25° 366 nm, pentane, -40°		176 65 65
	$\text{HC}\equiv\text{CBu-}n$	Pyrex, benzene, 70 h		168
	$\text{HC}\equiv\text{CBu-}n$	Pyrex, ether, 40 h		168
	$\text{C}(\text{Me})_2=\text{C}(\text{Me})\text{CH}_2$	—		174

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

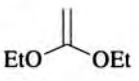
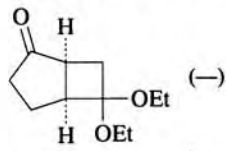
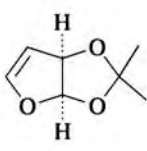
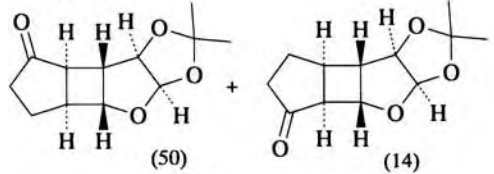
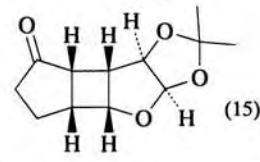

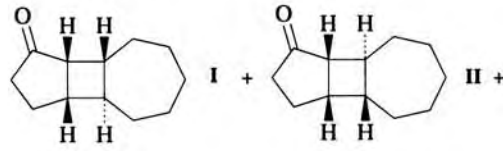
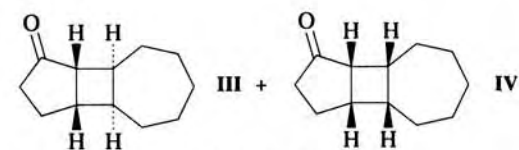
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, benzene, 10°, 24 h	 (—)	177
		—	 (50) + (14)	178
			 (15)	
		Pyrex, -78°	 I + II + 68	
			 III + IV	
			I:II:III:IV 4:22:6.7:1 (80-85)	

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

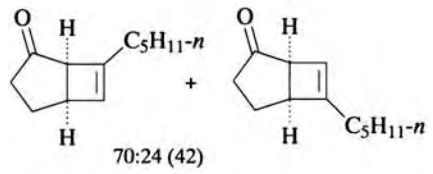
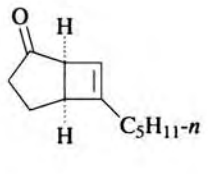
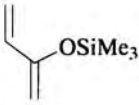
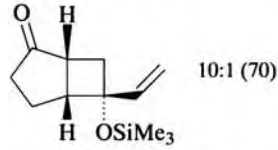
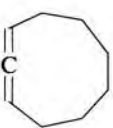
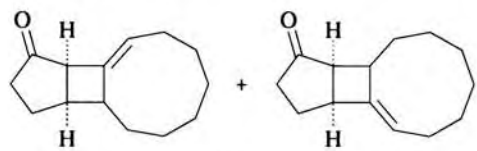
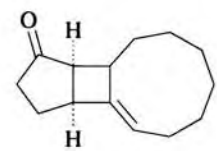
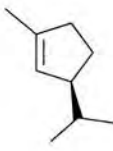
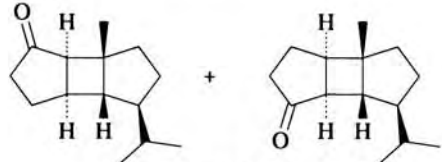
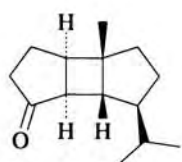
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{HC}\equiv\text{CC}_5\text{H}_{11-n}$	> 316 nm, neat, 58 h	 +  70:24 (42)	168, 179
		350 nm, benzene	 10:1 (70)	53
		Pyrex, ethanol	 +  16:5 (86)	174
		Pyrex, pentane	 +  1:1 (64)	180, 32

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, pentane, 25° 366 nm, pentane, -40°	 83:17 (65) 94:6 (65)	65
		Pyrex, benzene, 24 h	 (65)	59
		350 nm, pentane	 (40-50)	65, 181, 182
		366 nm, pentane	 (65)	183

TABLE II. CYCLOPENTENONE AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Hexanes	 (63)	184
		> 350 nm, hexane	 35:65 (60)	185

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES

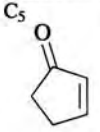
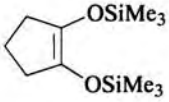
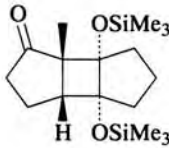
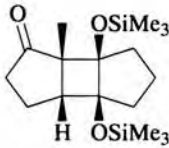
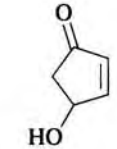
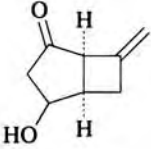
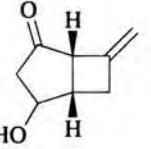
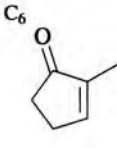
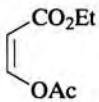
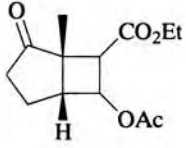
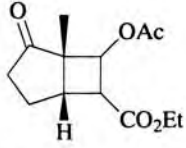
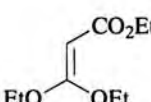
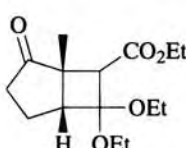
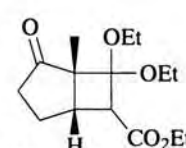
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, pentane	 +  (73)	183
	CH ₂ =C=CH ₂	Hexane	 +  37:63 (27)	184
		366 nm, 25° 366 nm, -40°	 +  76:24 (65-75) 62:38 (65-75)	65
		366 nm, 25° 366 nm, -40°	 +  84:16 (65-75) 92:8 (65-75)	65

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

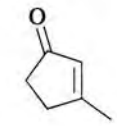
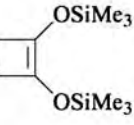
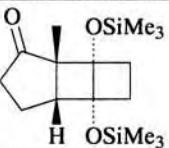
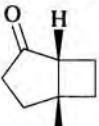
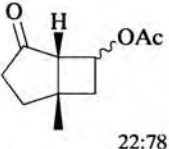
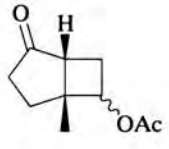
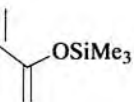
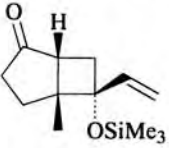
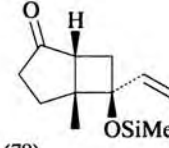
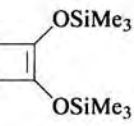
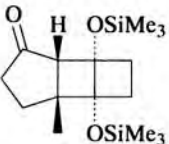
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, pentane	 (75-85)	66, 181, 182
	CH ₂ =CH ₂	Pyrex, CH ₂ Cl ₂ , -78°	 (85)	186
	CH ₂ =CHOAc	C ₆ H ₆ , 4-6°, 60 h	 +  22:78 (60)	187
		350 nm	 +  19:1 (79)	53
		350 nm, pentane	 (75-85)	66, 181, 182

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

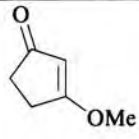
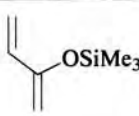
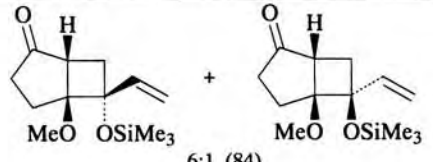
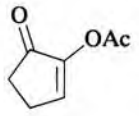

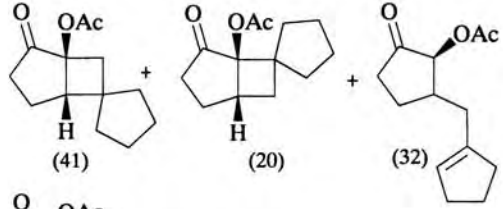
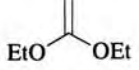
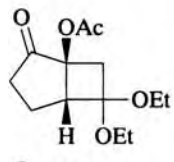
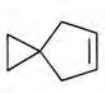
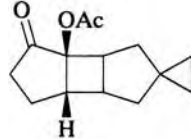
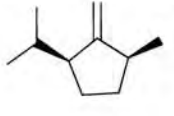
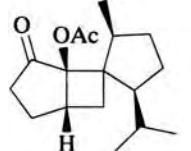
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm	 6:1 (84)	53
^{C7} 		Uranium, C ₆ H ₆ or CH ₃ CN	 (41) (20) (32)	188
		Pyrex, 3 h	 (-)	189
		Pyrex, ether	 (-)	190
		Pyrex, C ₆ H ₆	 (low)	80

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

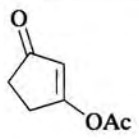
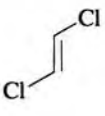
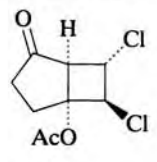

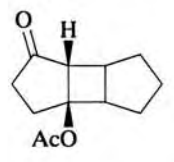
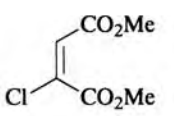
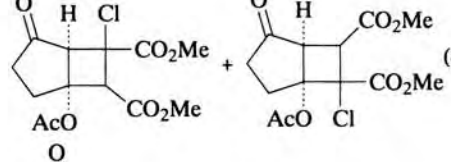
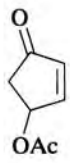
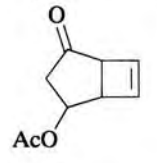
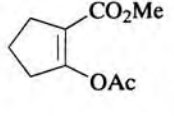
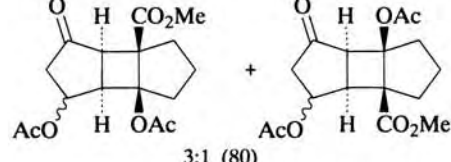
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, ether	 + isomers (-)	191
		Pyrex, ether	 (-)	191
		350 nm, dioxane, 40 h	 (80-85)	191
	HC≡CH	Acetone, -78°, 4 h	 (55)	192
		Pyrex, C ₆ H ₆ , 25°	 3:1 (80)	193

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

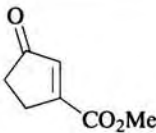

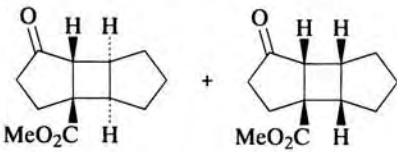
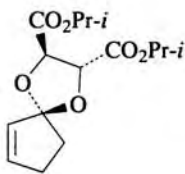
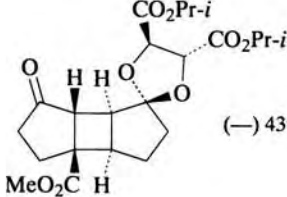
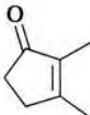
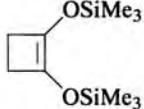
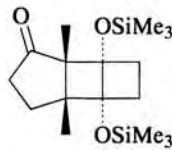
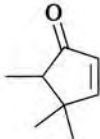

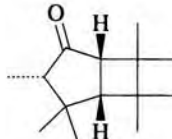
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, toluene, 60 h	 90:10 (78)	194, 195
		—	 (—) 43% de	196
		350 nm, pentane	 (75-80)	66, 181, 182
^{C₈} 		366 nm, CH ₃ CN	 (90)	197

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

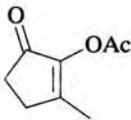
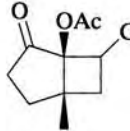
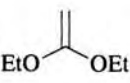
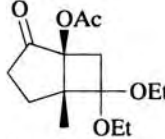
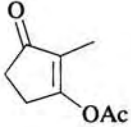

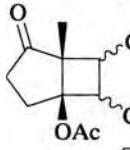
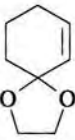
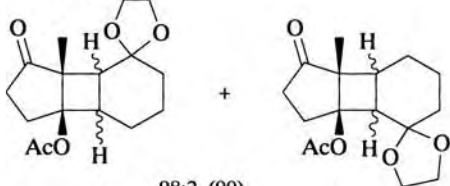
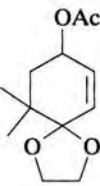
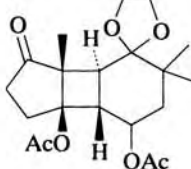
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =CHCN	Pyrex, THF:EtOH 7:2	 (16)	198
		Pyrex, 3 h	 (64)	189
		—	 (88)	199
		Pyrex, cyclohexane Pyrex, CH ₃ OH	 98:2 (90) 45:55 (—)	200 64
		Pyrex, cyclohexane, 60 h	 (35)	201, 202

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

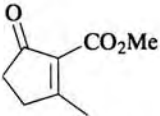

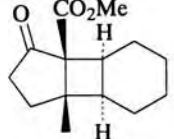
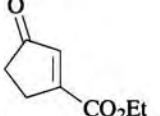
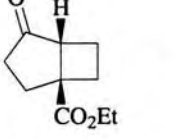
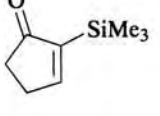
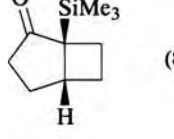
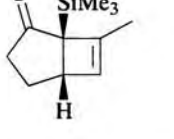
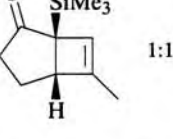
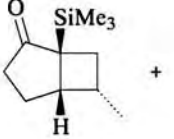
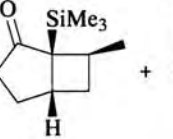
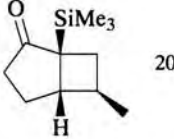
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, cyclohexane	 (—)	203
	CH ₂ =CH ₂	Pyrex, C ₆ H ₆ , 3.5 h	 (55)	204
	CH ₂ =CH ₂	Uranium, pentane, -78°, 16 h	 (80-90)	205
	HC≡CMe	Uranium, pentane	 +  1:1 (85)	205
	CH ₂ =CHMe	Uranium, pentane, 6 h	 +  +  20:47:33 (90)	205

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

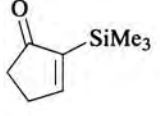

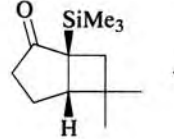
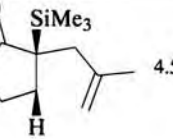
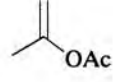
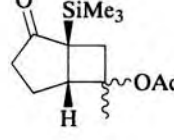
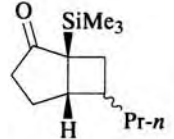
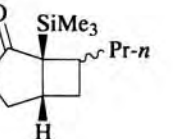

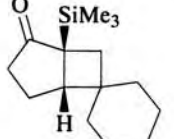
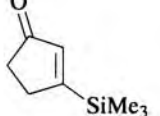
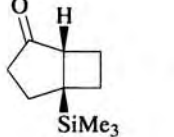
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Uranium, pentane, 6 h	 +  4.5:1 (89)	205
		Uranium, CH ₃ CN	 (74)	205
	CH ₂ =CHPr- <i>n</i>	Pentane	 +  (—)	205
		Uranium, pentane, 20 h	 (76)	205
	CH ₂ =CH ₂	—	 (91)	205

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

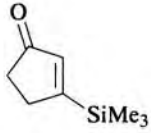

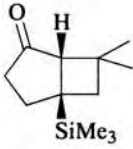
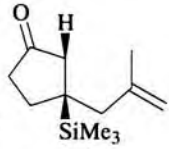
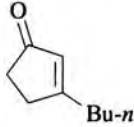
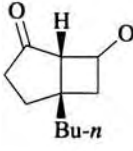
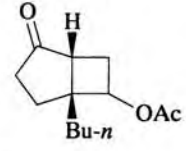
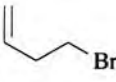
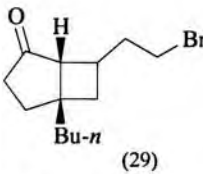
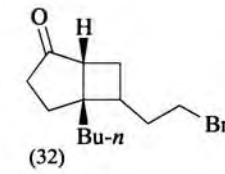
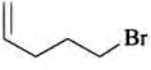
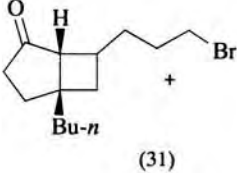
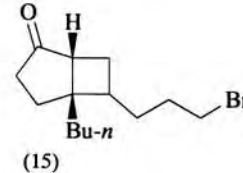
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Uranium, pentane, 6 h	 +  1:7 (90)	205
	CH ₂ =CHOAc	Cyclohexane Ether <i>n</i> -C ₁₁ H ₂₃ CO ₂ K, 0.08 eq	 +  25:75 (—) 26:74 (—) 51:49 (—)	56
		Pyrex, ethanol, 5 h	 (29) +  (32)	184
		Pyrex, ethanol, 5 h	 (31) +  (15)	184

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

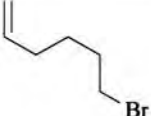
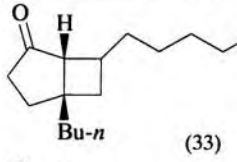
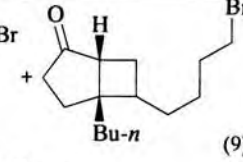
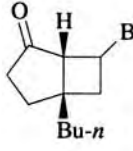
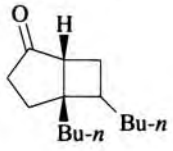
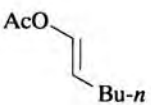
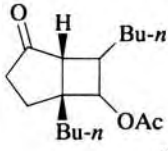
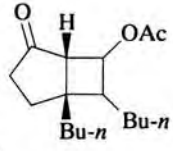
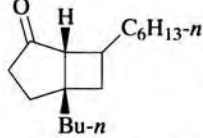
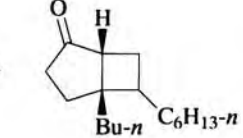
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, EtOH, 5 h	 (33) +  (9)	184
	CH ₂ =CHBu- <i>n</i>	Cyclohexane Ether <i>n</i> -C ₁₁ H ₂₃ CO ₂ K, 0.08 eq	 +  51:49 (—) 57:43 (—) 78:22 (—)	56
		Ether <i>n</i> -C ₁₁ H ₂₃ CO ₂ K, 0.08 eq	 +  0:100 (—) 70:30 (—)	56
	CH ₂ =CHCHC ₆ H ₁₃ - <i>n</i>	Cyclohexane CH ₃ CN <i>n</i> -C ₁₁ H ₂₃ CO ₂ K, 0.08 eq	 +  57:43 (—) 63:37 (—) 88:12 (—)	56

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Ether $n\text{-C}_{11}\text{H}_{23}\text{CO}_2\text{K}$, 0.08 eq	 0:100 (—) 70:30 (—)	56
		C_6H_6 $n\text{-C}_{11}\text{H}_{23}\text{CO}_2\text{K}$, 0.08 eq	 88:9 (—) 41:49 (—)	56
		—	(59)	199
		350 nm, cyclohexane	 12:1 (65)	96

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CHMe}$	—	 16:49:35 (—)	205
		—	(35)	206
	$\text{CH}_2=\text{CH}_2$	Pyrex, CH_2Cl_2 , -70° , 2 h	(—)	207
	$\text{CH}_2=\text{CH}_2$	Pyrex, CH_2Cl_2 , -70° , 2 h	 (30) + (16)	207

TABLE III. SUBSTITUTED CYCLOPENTENONES AND ALKENES OR ACETYLENES (Continued)

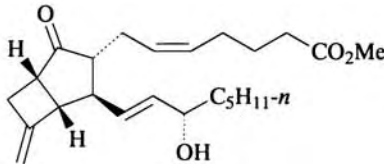
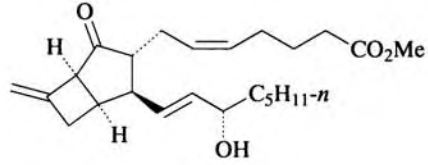
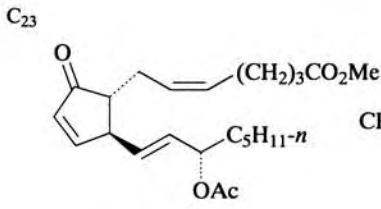
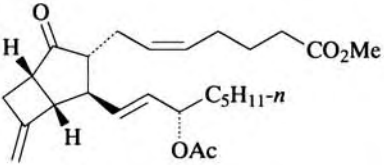
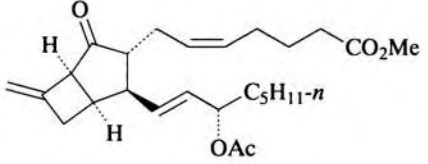
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, CH_2Cl_2 , -70° , 1 h	 (22) +	207
			 (19)	
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, CH_2Cl_2 , -70° , 80 min	 (16) +	207
			 (20)	

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES

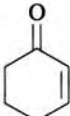
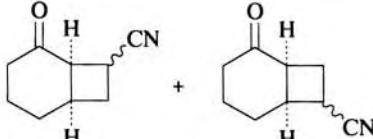
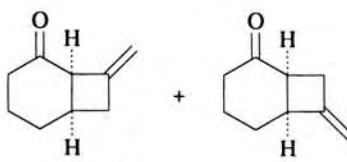
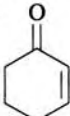

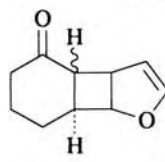
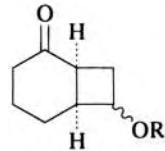
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$CH_2=CHCN$	Corex, pentane -78°	 61:39 (—)	28
	$CH_2=C=CH_2$	Pyrex, pentane Dichloromethane Dry silica gel	 (55) 94:6 (—) 65:35 (—)	28 208 208
		Pyrex, 5° , 3 h	 (63)	209
	$CH_2=CHOR$	R = Ac R = Bn	 (60) (65)	28,54 28

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)

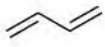
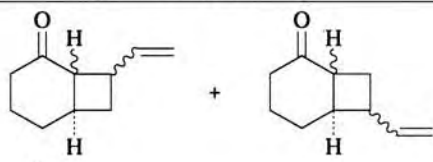
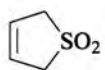
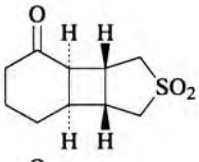

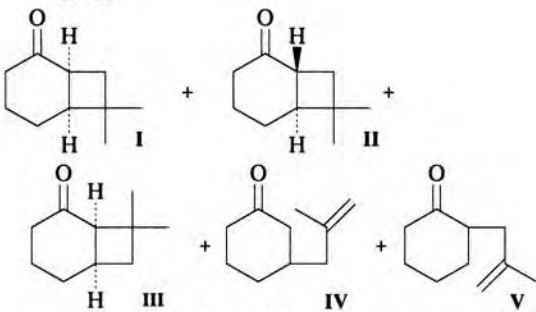
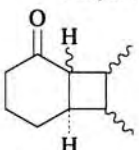
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, -25°, 4 h	 (72)	209
		CH ₃ CN, Vycor	 (23)	171
		Corex, pentane, 25° Corex, pentane, -40°	 I (6.5) + II (26.5) + III (6) + IV (8) + V (14) I:II, 1:4 (58) plus others	28 210
	<i>cis-</i> or <i>trans</i> -2-butene	Pyrex, pentane, 5 h	 (70)	28

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)

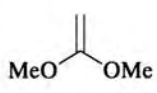
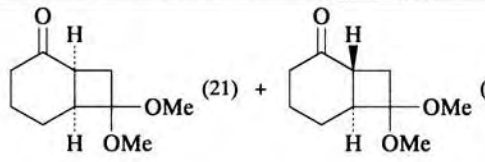
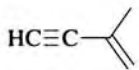
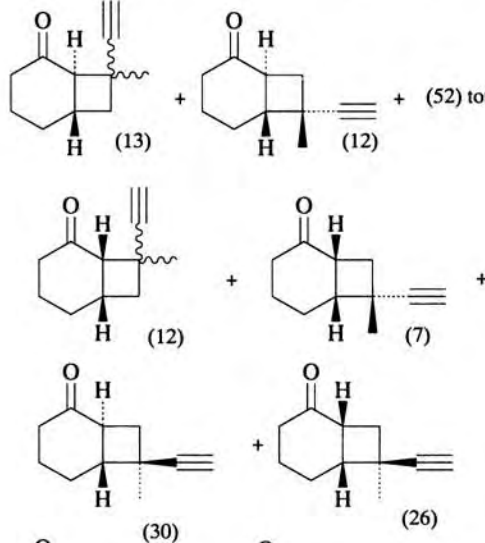

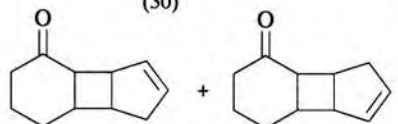
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, pentane	 (21) + (49)	28
		>300 nm, benzene	 (13) + (12) + (12) + (7) + (30) + (26)	211
		Pyrex, benzene, -25°, 4 h	 (47)	209

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)

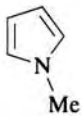
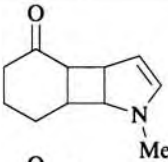
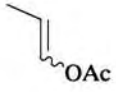
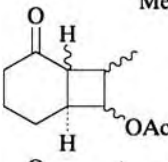
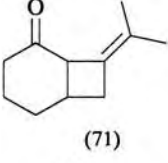
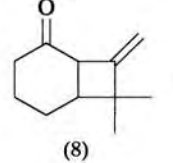
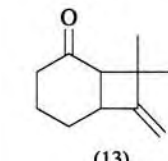
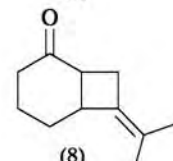

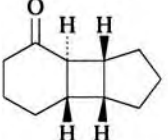
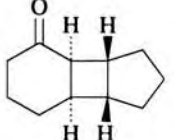
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, benzene, 5 h	 (—)	209
		—	 (—)	54
	$\text{C}=\text{CH}_2$	Pyrex, CH_2Cl_2 , 0°	 (71) +  (8)	120
			 (13) +  (8)	
		Corex, pentane, -78°	 +  30:70 (67)	28

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)


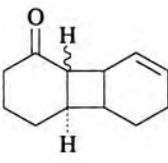
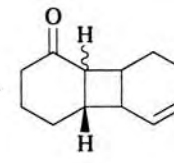
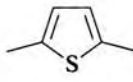
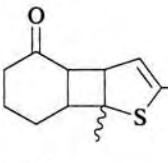
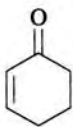
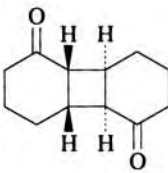
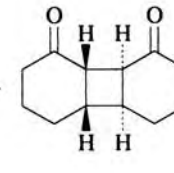
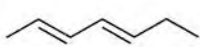
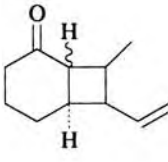
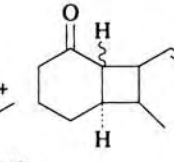
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, benzene, 4.5 h	 +  (16)	209
		Pyrex, benzene, 3 h	 (43)	209
		(—)	 +  1:2 (16)	173
		Pyrex, benzene	 +  (40)	209

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)

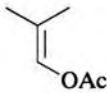
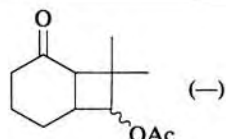
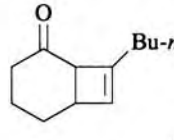
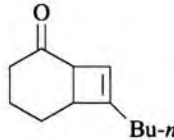
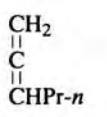
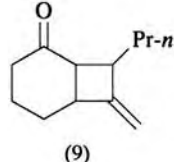
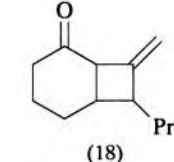
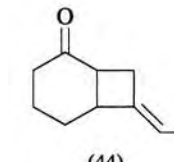
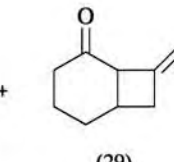
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		(-)	 (-)	54
	HC≡CBu- <i>n</i>	>300 nm, benzene, 7 h	 +  (30) 209 7:1 (28)	
		(-)	 (9) +  (18) +  (44) +  (29)	120

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)

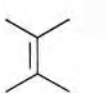
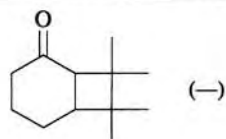

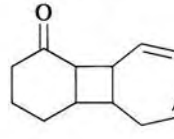
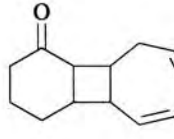

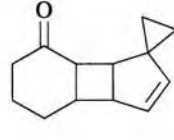
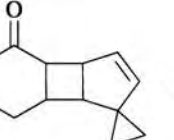
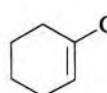
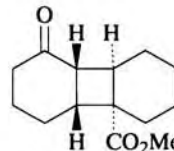

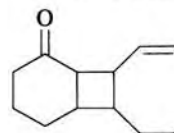
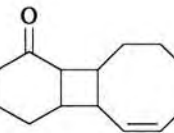
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, isooctane	 (-)	212
		Pyrex, benzene, 5°, 4.5 h	 +  (30)	209
		Pyrex, benzene	 +  (55)	209
		Pyrex, CH ₂ Cl ₂ , 5 h	 (7)	67
		Pyrex, benzene, 1.5 h	 +  (78)	209

TABLE IV. CYCLOHEXENONE AND ALKENES OR ACETYLENES (Continued)


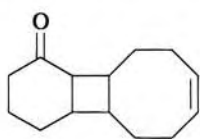
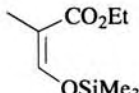
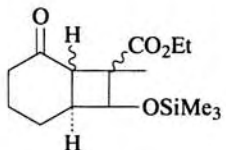
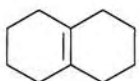
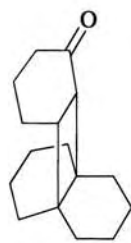
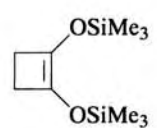
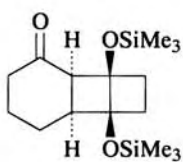
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, benzene, 3 h	 (66)	209
		Pyrex, benzene, 24 h	 (99)	59
		Pyrex, neat	 (13)	213
		350 nm, Rayonet, pentane	 (40-50)	182

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES

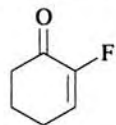

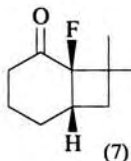
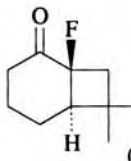
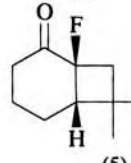
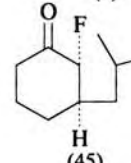
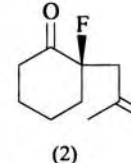
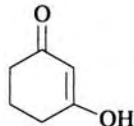
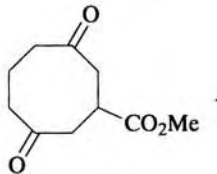
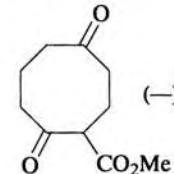
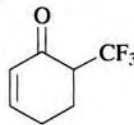

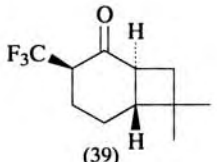
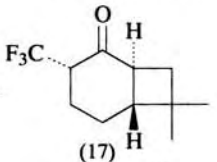
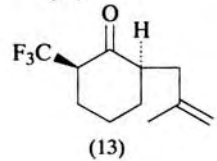
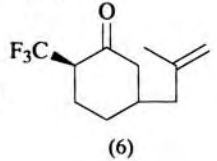
	Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆			Pentane, Pyrex, 0°	 (7) +  (8) +  (5) +  (45) +  (2)	214
		CH ₂ =CHCO ₂ Me	Pyrex, cyclohexane, 5 h	 +  (—)	191
C ₇			—	 (39) +  (17) +  (13) +  (6)	215

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	<i>trans</i> -ClCH=CHCl <i>cis</i> -ClCH=CHCl	Corex, ether, 7 h Corex, ether, 7 h	 (48) + (33) (22) (51)	216
	CH ₂ =CH ₂	Pyrex, benzene Benzene, 80 h	 (55) (40)	217 218
	CH ₂ =CHCN	Corex, ether, 2.5 h	 (9) + (29) + (17)	216
	CH ₂ =C=CH ₂	— -78°	 (9) + (100) 4:1 (—) 100:0 (100)	219 220, 221
		CH ₃ CN, Vycor	 (27) + (9)	171

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, 0°, 7 h	 (34) + (17) + (31) + (17)	222
	CH ₂ =CHOR	Pyrex, benzene Corex, 5 h	 (68) (90)	218 216
	R = Ac R = Et			
		Corex, ether, 2.5 h, 6°	 (26) + (38)	216
		—	 (14) + (50) + (27)	216

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)


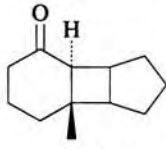
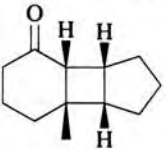
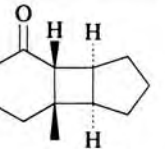
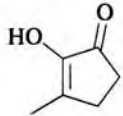
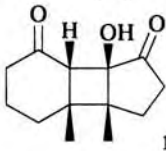
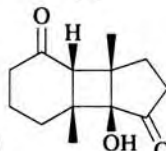

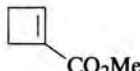
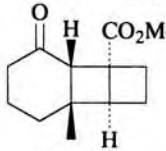
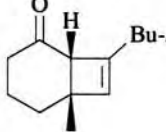
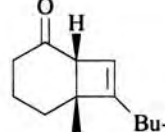
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, ether, 2 h	 +  + 	216
		Pyrex, ethanol, 10 d	 +  + 	223
		Pyrex, CH ₂ Cl ₂ , -78°	 (85)	50, 51, 52
	HC≡CBu- <i>n</i>	—	 +  5.5:1 (40)	168

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

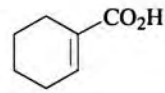
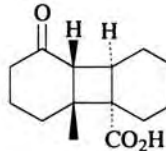

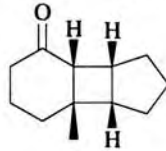
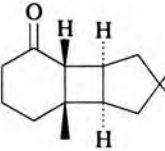
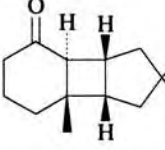
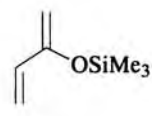
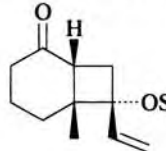
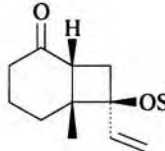
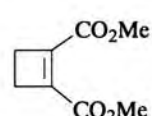
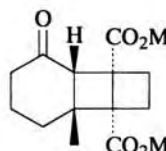
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, CH ₂ Cl ₂ , 8 h	 (9)	67
		Pentane, -10°	 (12) +  (72) +  (14)	224, 225
		350 nm, cyclohexane	 +  9:1 (63)	96
		350 nm, benzene, 22 h	 (70)	226

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, CH ₂ Cl ₂ , 8 h	 (74)	67
		Corex, 4.5 h	 (—)	216
		350 nm, Rayonet	 (75-80)	66
		C ₆ H ₁₂ CH ₂ Cl ₂ C ₆ H ₅ CH ₃ CH ₃ OH CF ₃ CH ₂ OH	 62% de 52% de 56% de 30% de 12% de	92, 227
R = 8-phenylmenthyl				

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, CH ₃ CN, 24-70 h	 (28) + (23) +	215
			 (10) + (20)	
	HC≡CBu- <i>n</i>	Benzene, 24 h, 25°	 1:1.4 (5)	168
		350 nm, Rayonet	 (trace)	66

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

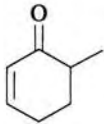

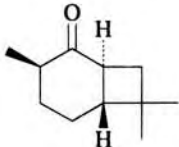
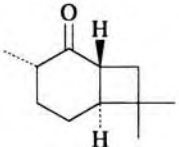
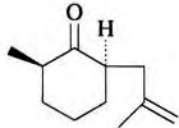
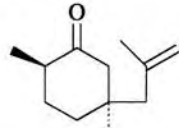

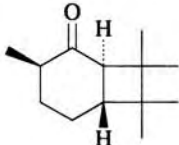
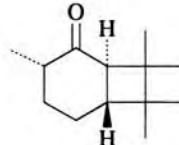
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, CH ₃ CN, 24-70 h	 (39) +  (17) +  (13) +  (6)	215
		350 nm, CH ₃ CN, 24-70 h	 (40) +  (28)	215

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

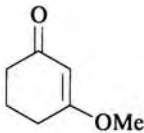
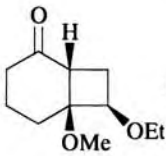
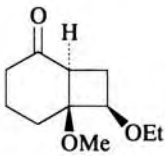
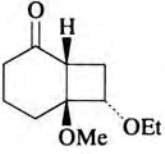
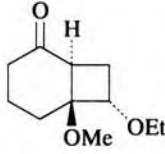
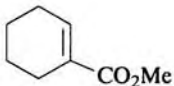
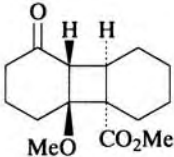
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =CHOEt	254 nm, CH ₃ OH	 I +  II +  III +  IV I:II = 39:1, III:IV = 4:1 (—)	228
		Acetophenone, 8 h	 (11)	67

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

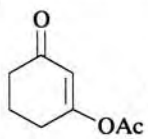
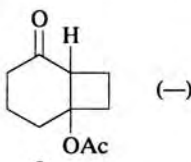
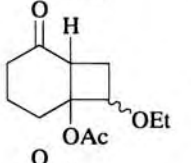
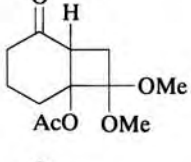

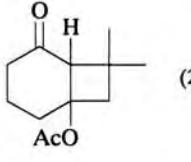
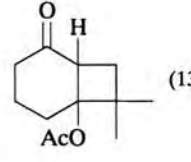
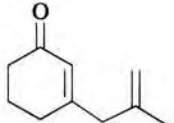
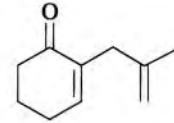
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 	$CH_2=CH_2$	Pyrex, -70 to -90°	 (—)	29
	$CH_2=CHOEt$	Ether, 18 h	 (44,17)	216
	$MeO-C(=CH_2)-OMe$	Pyrex, ether, 6 h	 (44)	216
		Ether, -15°, 36 h	 (25) +  (13) +	216
			 (21) +  (17)	

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)


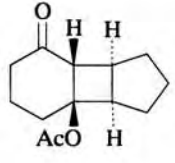
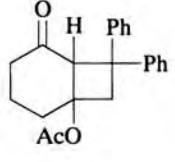
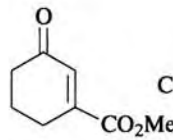
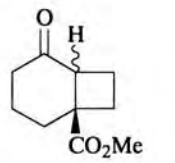

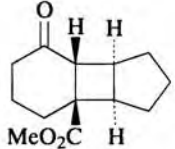
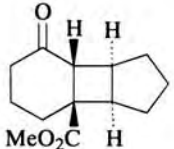
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Ether, 28 h	 (68)	216
	$Ph-C(=CH_2)-Ph$	Pyrex, ether, 18 h	 (low)	216
	$CH_2=CH_2$	Benzene	 (82)	230, 229
		350 nm, toluene, 93 h	 +  90:10 (91)	92, 194, 195

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{HC}\equiv\text{CBu-}n$	Benzene, 25°, 2 h		168
		—	<p> X = CO₂Me 43% de X = CO₂Et 64% de X = CO₂Pr-<i>i</i> 84% de X = CH₂OBn 12% de </p>	196
	<p>R = (-)-3-menthyl</p>	355 nm		231

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, CH ₃ CN	<p> X = F (25) (63) X = Cl (43) (56) </p>	197
		366 nm, isooctane, 50 h 366 nm, cyclohexane	<p> X = F 0:10:90 (—) X = Cl 12:55:0 (—) </p>	212 197
		Pyrex, ether, 28 h		200, 191
		350 nm, Rayonet		66

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

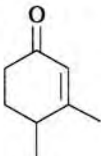
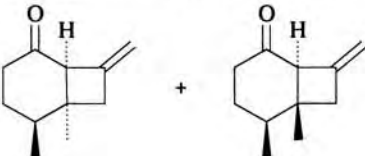
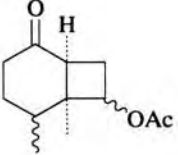
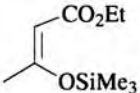
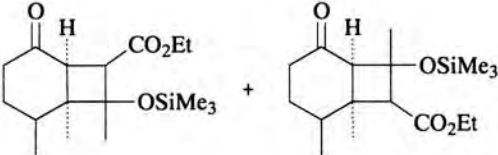
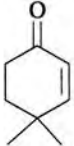
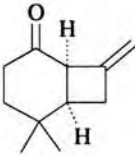
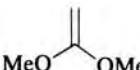
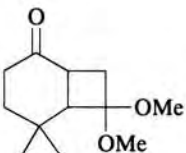
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =C=CH ₂	Pyrex, ether, -78°, 24 h	 4:1 (72)	75
	CH ₂ =CHOAc	C ₆ H ₆ , 6 h	 (—)	54
		Pyrex, C ₆ H ₆ , 24 h	 3:1 (75)	59
	CH ₂ =C=CH ₂	Pentane, -78°, 15 h	 (20)	221
		—	 (78)	60

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

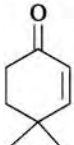

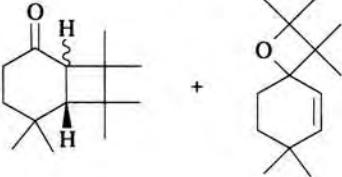

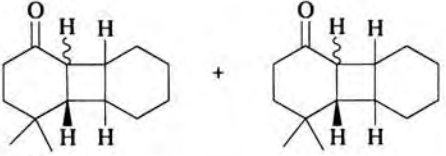
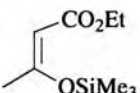
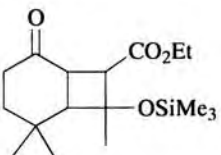
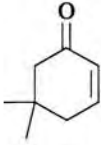
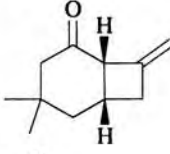
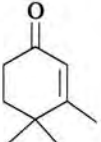
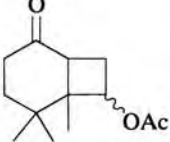
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		366 nm, <i>n</i> -octane	 48:52 (—)	212, 232
		Corex, 48 h, 10° Hexane, Rayonet, 24 h	 70:30 (—)	233, 234
		Pyrex, C ₆ H ₆ , 20 h	 (90)	59
	CH ₂ =C=CH ₂	Pentane, -78°, 5 h	 (45)	221
^{C₉} 	CH ₂ =CHOAc	—	 (80)	60

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

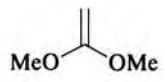
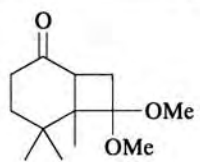
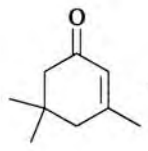
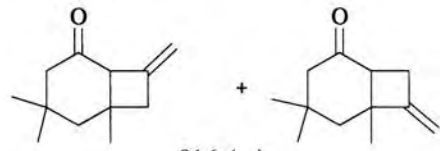
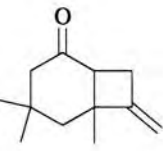
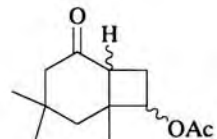
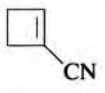
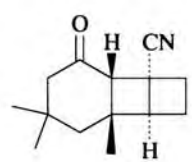
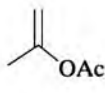
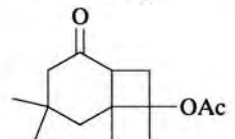
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 20 h	 (71)	60
	CH ₂ =C=CH ₂	CH ₂ Cl ₂ Dry silica gel	 +  94:6 (—) 52:48 (—)	208
	CH ₂ =CHOAc	C ₆ H ₆ , 60 h	 (85)	54
		Pyrex, CH ₂ Cl ₂ , 0°	 (85)	57, 58
		Pyrex, CH ₃ OH, 0°, 6.5 h	 (71)	235

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

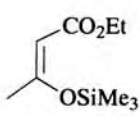
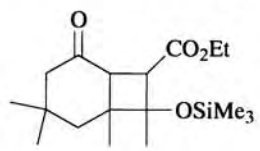
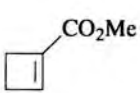
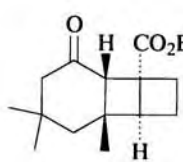
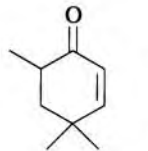

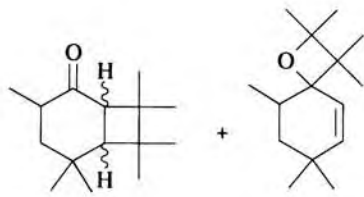
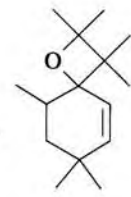

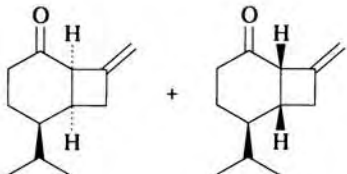
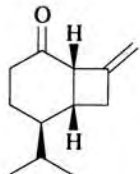
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 24 h	 (100)	59
		Pyrex, ether, 15 h	 (38)	236
		366 nm, isooctane, 50 h	 +  70:30 (—)	212
	CH ₂ =C=CH ₂	Pyrex, ether	 +  1:4 (72)	237, 238

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

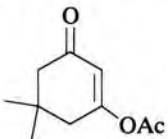

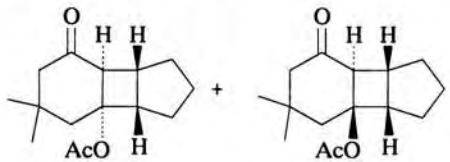

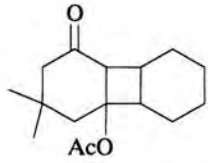
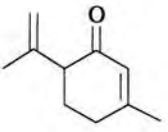
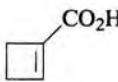
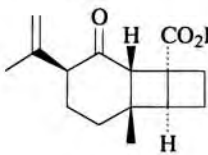
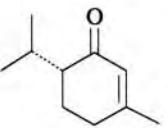
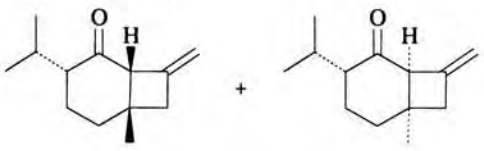
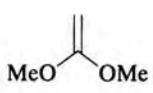
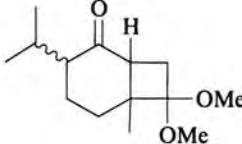
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.		
		Pyrex, 0°, 15 h		2:1 (65)	239	
		Pyrex, 24 h		(-)	191	
			350 nm, C ₆ H ₆		(40)	240
		CH ₂ =C=CH ₂	-78°		3:1 (100)	220, 241
		-		(-)	242	

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)



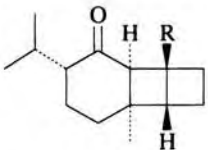
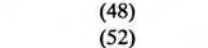
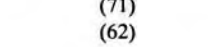
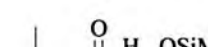
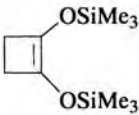
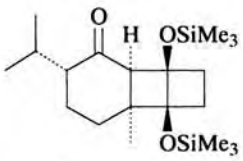
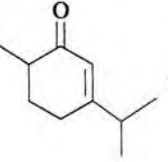
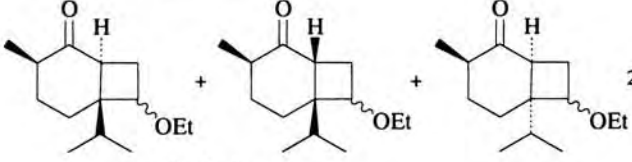
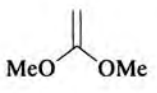
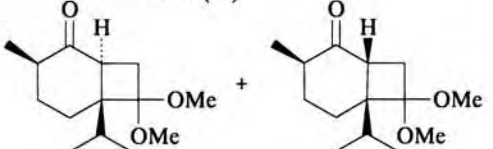
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
		Ether, 16 h		(48)	236
		350 nm C ₆ H ₆		(52)	243
		-78°, quartz		(71)	89
		350 nm, C ₆ H ₆		(62)	51, 164, 244
		350 nm, Rayonet		(75-80)	245
	CH ₂ =CHOEt	Pyrex, C ₆ H ₆ , 6 h		2:7:1 (-)	246, 246
		Pyrex, C ₆ H ₆ , 10 h		1:4 (80)	246

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 30 h	(12)	246
		Pyrex, ether, 30 h	(10)	246
		Pyrex, C ₆ H ₆ , 20 h	+ 2:1 (90)	246
		Pyrex, C ₆ H ₆ , 30 h	+ (60)	246

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CBu- <i>n</i>	>300 nm, C ₆ H ₆ , 8 h	+ 1:4.2 (55)	168
		Pyrex, C ₆ H ₆ , 30 h	+ 5:1 (37)	246
	CH ₂ =CH ₂	Pyrex, CH ₂ Cl ₂ , -78°	+ + (—)	87
		Ether, 40-80 h	(65)	247

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

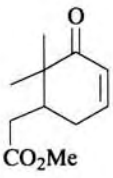
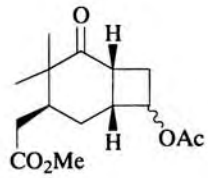
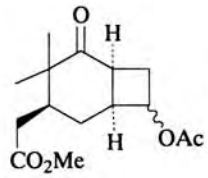
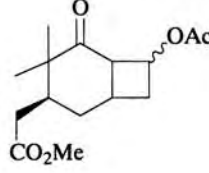
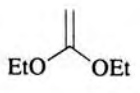
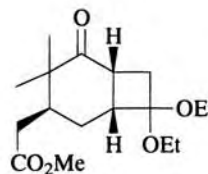
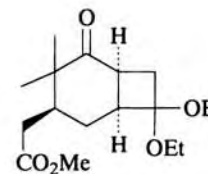
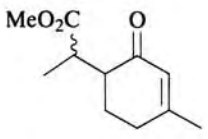
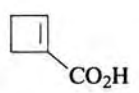
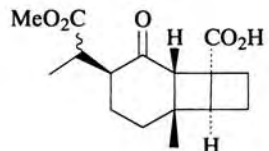
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CHOAc}$	Pyrex, C_6H_6 , 3 h	 +  +  1.8:2.2:1 (77)	90
		Pyrex, C_6H_6	 +  3:5 (96)	90
		350 nm, toluene	 (—)	248

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

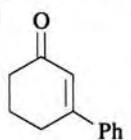
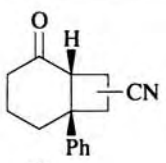
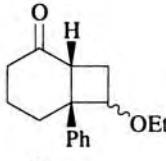
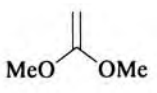
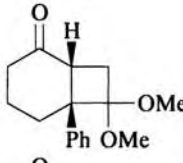

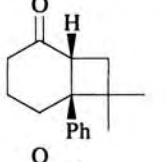

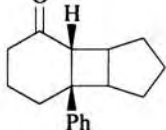
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	$\text{CH}_2=\text{CHCN}$	Pyrex, ether, 7 h	 (—)	216
	$\text{CH}_2=\text{CHOEt}$	Pyrex, ether, 5 h	 (78)	216
		Pyrex, ether, 3 h	 (71)	216
		Pyrex, ether, -20° , 5 h	 (45)	216
		Pyrex, ether, 8 h	 (38)	216

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

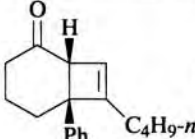
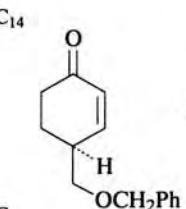
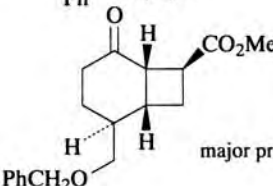
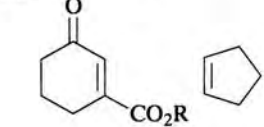

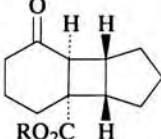
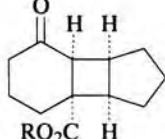
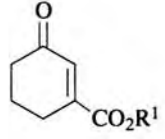
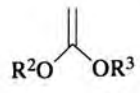
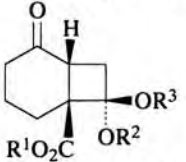
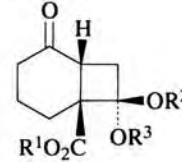
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{HC}\equiv\text{CC}_4\text{H}_9\text{-}n$	$>300\text{ nm, C}_6\text{H}_6$	 (45)	168
	$\text{CH}_2=\text{CHCO}_2\text{Me}$	Uranium, $\text{CH}_2\text{Cl}_2, 4^\circ$	 (> 49) major product	215
		—	 I +  II R = bornyl I (83), 4% de + II (17) R = menthyl I (70), 18% de + II (30), 25% de	92
		—	 I +  II R ¹ R ² R ³	231
			(-)-3-menthyl Et Et I 14% de + II — (—) (+)-3-menthyl Et Et I 16% de + II — (45) (-)-3-menthyl Me (-)-3-menthyl I 45% de + II 40% de (52) (+)-3-menthyl Me (-)-3-menthyl I 17% de + II 12% de (48)	

TABLE V. SUBSTITUTED CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

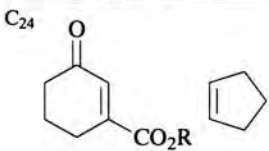

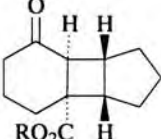
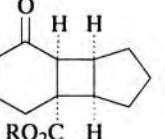
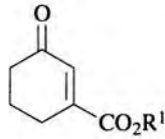
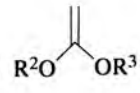
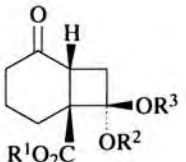
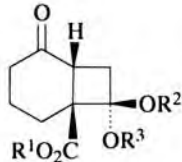
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 I +  II	227
	Equiv. 2.0 1.5 1.5 1.5 1.5 1.5 1.5		R = 8-phenyl-3-menthyl I (60) 30% de + II (40) 79% de I (—) 32% de + II (—) I (—) 37% de + II (—) 68% de I (—) 49% de + II (—) 79% de I (—) 51% de + II (—) 78% de I (—) 68% de + II (—) I (—) 68% de + II (—) 76% de I (—) 56% de + II (—) 78% de	
		—	 I +  II R ¹ R ² R ³	231
			(-)-8-phenyl-3-menthyl Et Et I 56% de + II — (—) (+)-iso-8-phenyl-3-menthyl Et Et I 46% de + II — (46) (-)-8-phenyl-3-menthyl Me (-)-3-menthyl I 74% de + II 72% de (55) (+)-iso-8-phenyl-3-menthyl Me (-)-3-menthyl I 9% de + II 22% de (50)	

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES

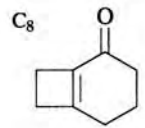
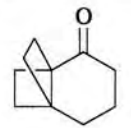
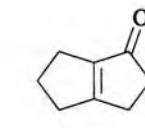
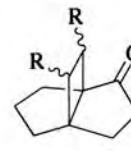
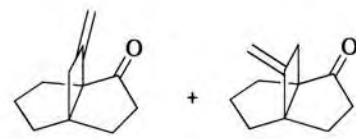
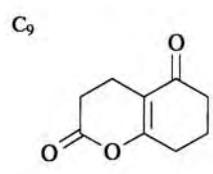
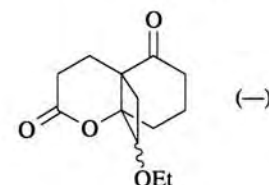
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CH}_2$	Pyrex, -70°	 (50)	29
	$\text{RCH}=\text{CHR}$			
	<u>R</u>			
	Cl	Pyrex, CH_2Cl_2 , 5 h	(77)	249
	Me (<i>trans</i>)	Pyrex, CH_2Cl_2 , -70°	(65)	250,251
	Me (<i>cis</i>)	Pyrex, CH_2Cl_2 , -70°	(62)	250,251
	$(\text{CH}_2)_4$	Corex, CH_2Cl_2 , 5 h	(69)	186,249, 251,252
	$\text{CH}_2=\text{C}=\text{CH}_2$			
		CH_2Cl_2	61:39 (—)	208
		Dry silica gel	46:54 (—)	208
	$\text{CH}_2=\text{CHOEt}$	—	 (—)	204

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

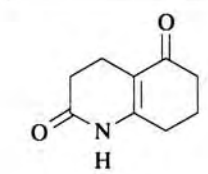
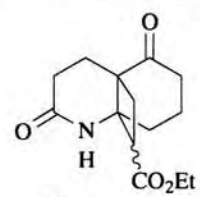
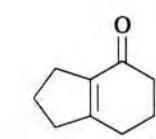
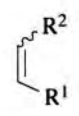
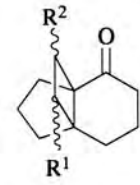
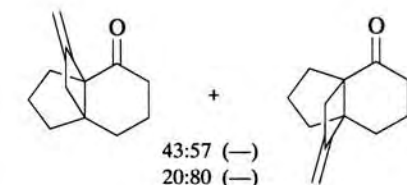
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CO}_2\text{Et}$	Pyrex, 0° , 2 d	 (50)	253
				
	<u>R¹</u> <u>R²</u>			
	Cl Cl	Corex, pentane, 30 min	(77)	254
	Cl Cl	Pyrex, 40 h	(41)	254
	H H	Pyrex, CH_2Cl_2 , -78° , 17 h	(86)	255
	OAc H	Ether, -78° , 3.5 h	(91)	256
	Me Me (<i>cis</i>)	Pyrex, CH_2Cl_2 , -70°	(97)	186,251
	Me Me (<i>trans</i>)	Pyrex, CH_2Cl_2 , -70°	(99)	186,251
	$-(\text{CH}_2)_4-$	Pyrex, CH_2Cl_2 , 25°	(71)	186,251
	$\text{CH}_2=\text{C}=\text{CH}_2$			
		CH_2Cl_2	43:57 (—)	208
		Dry silica gel	20:80 (—)	208

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	MeC≡CMe	Corex, pentane, 30 min	 (67)	254
		Pyrex, hexane, -50°, 8 h	 (41)	255
	CH ₂ =C=CH ₂	CH ₂ Cl ₂ Dry silica gel	 + 75:25 (—) 32:68 (—)	208 208
		R H Me (<i>cis</i>) Me (<i>trans</i>) -(CH ₂) ₄ -	 (—) (83) (84) (84)	257 251 251 186,251

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =CH ₂	—	 (77)	258
	CH ₂ =C=CH ₂	Pyrex, C ₆ H ₆	 (85)	84
^{C₁₀} 	CH ₂ =C=CH ₂	THF, -80°	 + 1:1 (50)	253
	CH ₂ =C=CH ₂	CH ₂ Cl ₂ , -78°	 + 4.5:1 (94)	250
	CH ₂ =C=CH ₂	Pyrex, C ₆ H ₆	 (75)	84

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane, -50°	(41) 10:1 β:α	255
		Pyrex, 25°	(92)	252
	R			
	Cl	Pyrex	(94)	259
	H	Pyrex, C ₆ H ₆ , 25°	(30)	260
	(CH ₂) ₅	Pyrex, neat	(69)	260
	<i>i</i> -PrPr- <i>i</i>	Pyrex, neat	(77)	260
	(CH ₂) ₆	Pyrex, neat	(49)	260
	CH ₂ =C=CH ₂		+	
		CH ₂ Cl ₂	70:30 (—)	208
		Dry silica gel	34:66 (—)	208

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	R			
	H	Pyrex, CH ₂ Cl ₂ , -78°	(78)	186
	Me (<i>cis</i>)	Pyrex, CH ₂ Cl ₂ , -78°	(48)	251,186
	Me (<i>trans</i>)	Pyrex, CH ₂ Cl ₂ , -78°	(47)	251,186
	-(CH ₂) ₄ -	Pyrex, CH ₂ Cl ₂ , -78°	(12)	251,186
^C ₁₁ 		Pyrex, hexane, -50°	(74) 2:1 β:α	255
	CH ₂ =C=CH ₂	—	(—)	261
	CH ₂ =C=CH ₂	—	(—)	261

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, THF, -78° , 8 h	(87)	262
	$\text{CH}_2=\text{CH}-\text{OAc}$	Pyrex, THF, -78° , 6 h	+ 1:1 (91)	262
		Pyrex, 25°	(87)	252
C_{12} 	$\text{MeO}-\text{C}(\text{Me})=\text{C}(\text{Me})-\text{OMe}$	—	(81)	60

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{C}=\text{CH}_2$	THF, -70°	(100)	263, 264
	$\text{CH}_2=\text{CH}_2$	Pyrex, -78°	(—)	265
	$\text{CH}_2=\text{C}=\text{CH}_2$	Corex, hexane, -78° , 6 h	(75)	266
		Pyrex, cyclohexane	(50)	72, 73
		Pyrex, cyclohexane	(50)	72, 73

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{ClCH}=\text{CHCl}$	—	(—)	267
	$\text{CH}_2=\text{CH}_2$	0° , 5 h	(62) + (24)	192
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, hexane, THF, -80° , 2 h	(83)	268
		Pyrex	(—)	190

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, cyclohexane	(5)	72, 73
		Pyrex, cyclohexane	(55)	72, 73
		300 nm, cyclohexane	10:1 (72)	53
	$\text{CH}_2=\text{C}=\text{CH}_2$	THF, -78° , Pyrex, 12 h	(83)	269

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, CH ₃ CN, 136 h	(38) + (32) + 270	270
			(13)	
		Pyrex, CH ₃ CN, 43 h	(38)	270
	CICH=CHCl	—	(49)	267

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	CICH=CHCl	—	(73)	267
C ₁₆ 		Pyrex, CH ₂ Cl ₂ , -78°	(56)	271
	CH ₂ =C=CH ₂	CH ₃ OH, -70°, 1.25 h SiO ₂ , 20°, 5 h	(53) + (54)	78:22 (53) 59:41 (—) 272
		Pyrex, THF, -70°	(58)	1:1 (58) 273

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CH}-\text{OAc}$	Pyrex, THF, 25°, 2 h	 (60)	274
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, THF, -80°, 13 h	 (-)	275
	$\text{CH}_2=\text{C}=\text{CH}_2$	Pyrex, THF, -78°, 18 h	 (80)	276
	$\text{CH}_2=\text{C}=\text{CH}_2$	EtOH, -78°, 4 h	 (65) + isomers (8)	277

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{ClCH}=\text{CHCl}$	-	 (-)	278
	$\text{CH}_2=\text{CH}_2$	Pyrex, CH_2Cl_2 , -78°, 1 h	 (-)	278
	$\text{CH}_2=\text{C}=\text{CH}_2$	Corex, hexane, -70°, 1 h	 (-)	219, 220, 279
	$\text{CH}_2=\text{CH}-\text{OAc}$	-	 (-)	278

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

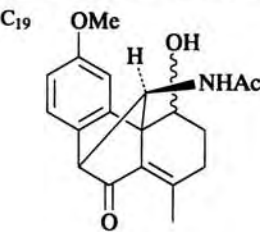
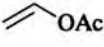
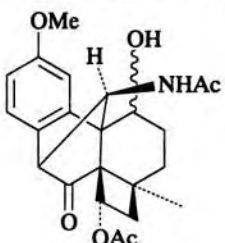
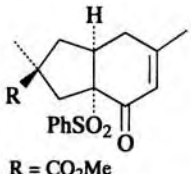
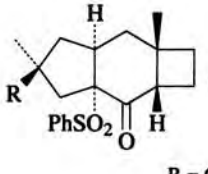
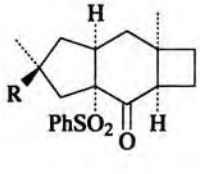
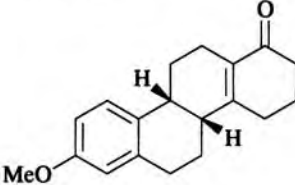
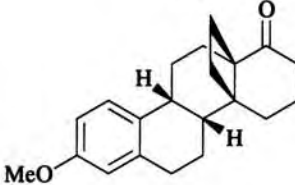
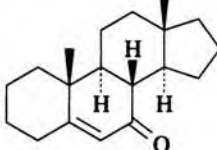
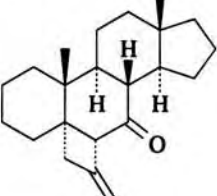
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 <p>C₁₉</p>		Pyrex, THF, -20°, 12 h	 <p>(89)</p>	276
 <p>R = CO₂Me</p>	CH ₂ =CH ₂	350 nm, CH ₂ Cl ₂ , -47°	 <p>(71) +</p>  <p>(23)</p>	280
	CH ₂ =CH ₂	Pyrex, CH ₂ Cl ₂ , -60°, 1 h	 <p>(82)</p>	281
	CH ₂ =C=CH ₂ —		 <p>(100)</p>	220

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

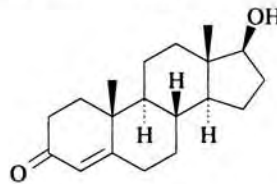
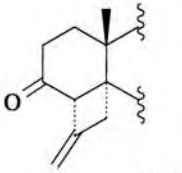
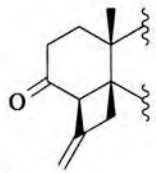
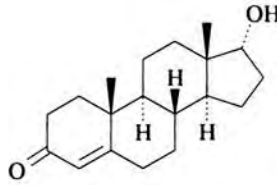
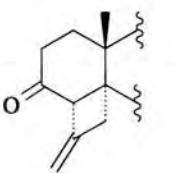
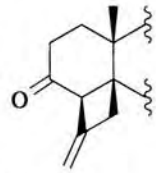

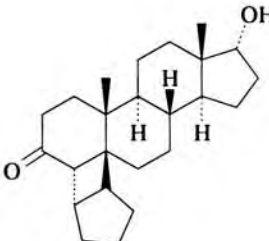
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =C=CH ₂	CH ₃ OH, 1.5 h, 20° SiO ₂ , 6 h, 20° Al ₂ O ₃ , 6 h, 20°	 <p>+ </p>  <p>82:18 (73) 59:41 (85) 61:39 (80)</p>	272
	CH ₂ =C=CH ₂	CH ₃ OH, 45 min, -70° SiO ₂ , 1.5 h, 20° Al ₂ O ₃ , 45 min, 20°	 <p>+ </p>  <p>92:8 (100) 34:66 (100) 6:94 (100)</p>	272
		Pyrex, dioxane, 30°, 19 h	 <p>(50)</p>	282

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

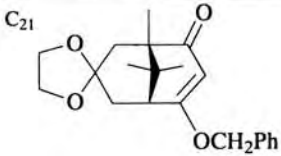

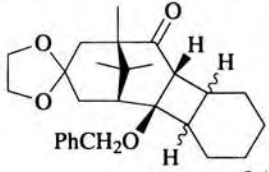
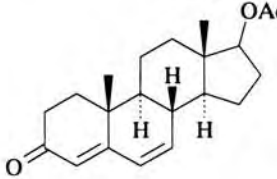
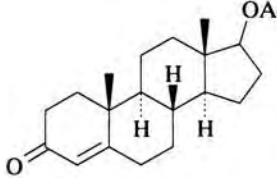
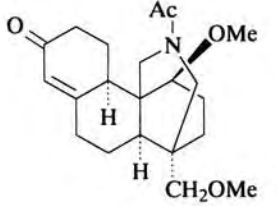
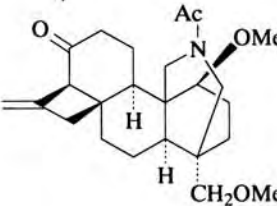
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, CH ₂ Cl ₂ , -78°	 (65)	271
	CH ₂ =CH ₂	Pyrex	(—)	283
	CH ₂ =C=CH ₂ -78°		(—)	220
	CH ₂ =C=CH ₂	Pyrex, THF, -80°	 (99)	261

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

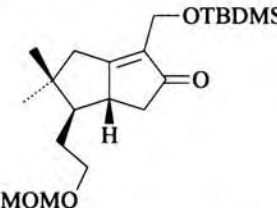
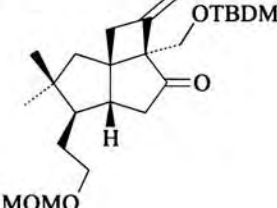
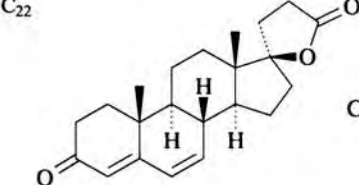
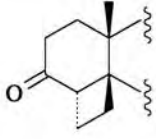

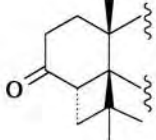

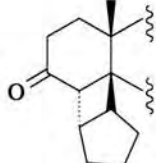
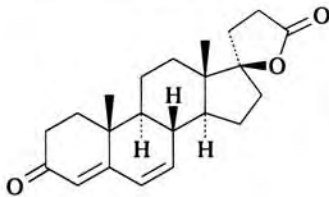

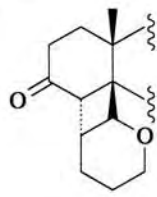
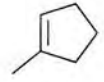
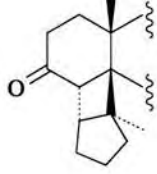
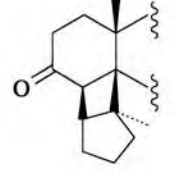

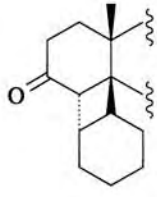
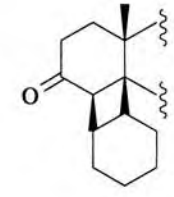
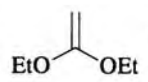
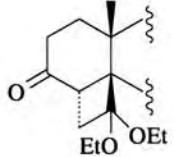
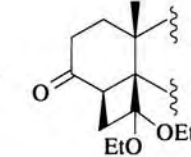
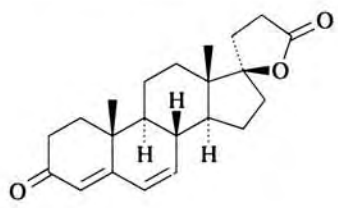

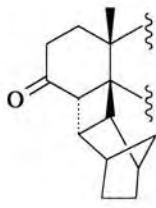
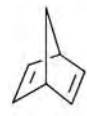
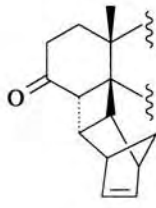

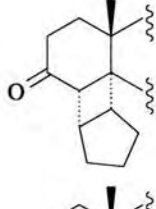

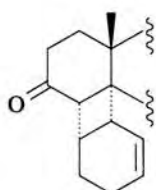
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	CH ₂ =C=CH ₂	THF, hexane, -78°	 (84)	284
	CH ₂ =CH ₂	Pyrex, C ₆ H ₆ , 50 h	 (6)	285
		Corex, C ₆ H ₆ , 4.5 h	 (90)	285
		Pyrex, EtOAc, 16 h	 (—)	285

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, EtOAc, 24 h	 (50)	285
		Pyrex, EtOAc, 4.5 h	 +  (—)	285
		Pyrex, EtOAc, 40 h	 +  1:1.5 (25)	285
		Pyrex, EtOAc, 17 h	 +  3:1 (70)	285

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TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, EtOAc, 5 h	 (61)	286
		Pyrex, EtOAc, 27.5 h	 (8)	286
		—	 (30)	287
		—	 (29)	287

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TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (*Continued*)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, EtOAc, 3 h	(30)	287
		EtOAc, 9 h	+ (35)	285
		EtOAc, 3 h	(40) + (15) + (25) + (12)	285

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TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (*Continued*)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, EtOAc, 12 h	(41)	286
		Pyrex, 3.5 h	(10)	286
		C ₆ H ₆ , 20°, 9.5 h SiO ₂ , 20°, 18 h	(82) (57)	282 272

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TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

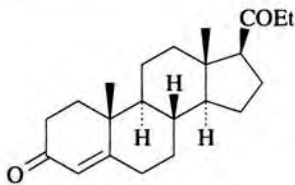
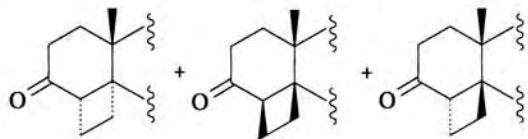
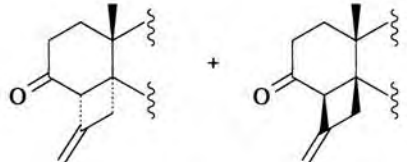
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{CH}_2$			
		CH_3OH , 1 h, 11°	57:10:32 (57)	288
		EtOAc , 4 h, 11°	67:33:0 (90)	288
		CH_3OH , 1 h, -78°	82:12:6 (24)	288
		EtOAc , 4 h, -78°	87:13:0 (100)	288
		SiO_2 , 4 h	49:51:tr (100)	288
		SiO_2 , -70° , 6 h	42:58:0 (96)	288
C_6H_6 , dioxane, 0° , 4 h	72:0:28 (64)	282		
	$\text{CH}_2=\text{C}=\text{CH}_2$			272
		CH_3OH , 30 min, 11°	83:17 (58)	
		EtOAc , 4 h, 11°	84:16 (100)	
		CH_3OH , 1 h, -78°	90:10 (75)	
		EtOAc , 1 h, -78°	89:11 (100)	
		SiO_2 , 2 h, 11°	46:54 (80)	
		SiO_2 , 3 h, -78°	47:53 (97)	
Al_2O_3 , 3 h, 11°	20:80 (80)			

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)


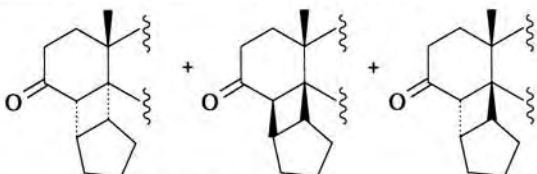
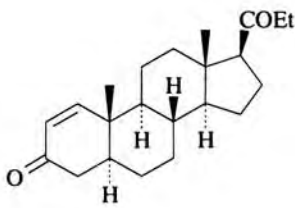

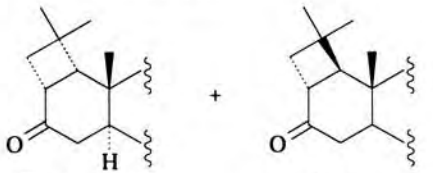

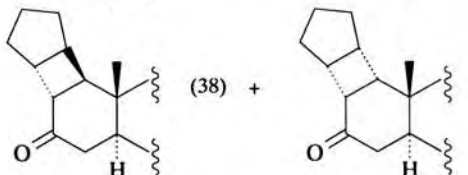
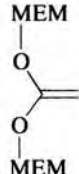
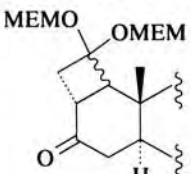
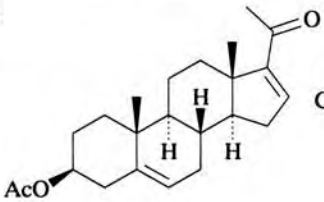
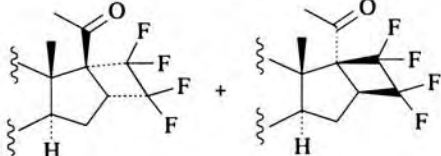
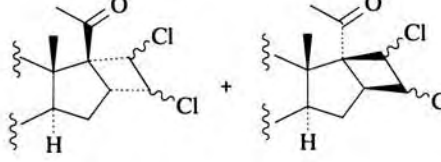
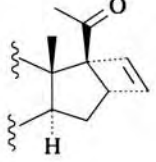
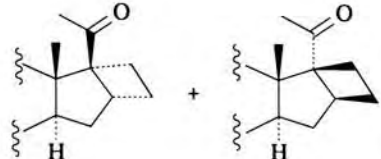
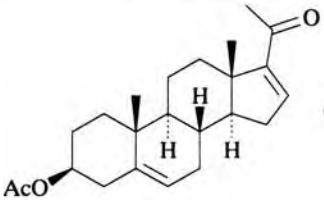
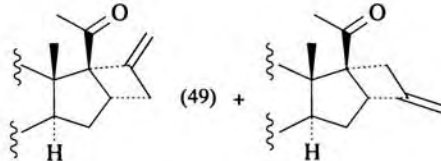
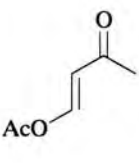
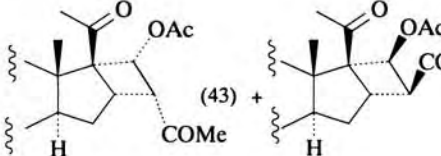
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.	
					
		CH_3OH , 1.6 h, 8°	46:22:31 (61)	288	
		Neat, 3 h, 8°	35:15:49 (100)	282	
		CH_3OH , 1.8 h, -70°	53:41:6 (67)	288	
		SiO_2 , 3 h, 11°	33:56:10 (52)	288	
SiO_2 , -78° , 7.5 h	32:57:10 (66)	288			
		Pyrex, EtOAc, -78° , 17 h		(—) 289	
		Pyrex, EtOAc, 1.25 h			(38) + (56) 289
				Pyrex, EtOAc, 32 h	

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
	CF ₂ =CF ₂	Pyrex, C ₆ H ₆ , 24 h	 2:1 (40)	290
	ClCH=CHCl	Pyrex, C ₆ H ₆ , 24 h	 1.1:1 (46)	290
	HC≡CH	Pyrex, C ₆ H ₆ , 24 h	 (25)	290
	CH ₂ =CH ₂	Pyrex, C ₆ H ₆ , 24 h	 7:1 (60)	290

420

TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
	CH ₂ =C=CH ₂	Pyrex, C ₆ H ₆ , 24 h	 (49) + (2)	290
		C ₆ H ₆ , 4 h, 20°	 (43) + (18)	290

421

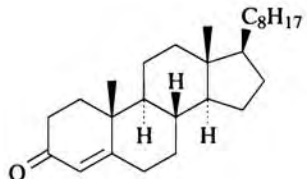
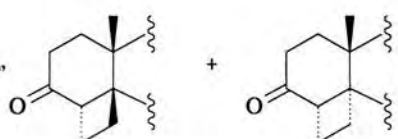
	CH ₂ =CH ₂	Dioxane, C ₆ H ₆ , 4°, 8 h	 (-)	282
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TABLE VI. POLYCYCLIC CYCLOHEXENONES AND ALKENES OR ACETYLENES (Continued)

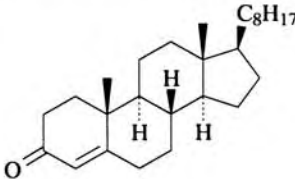
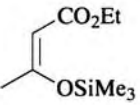
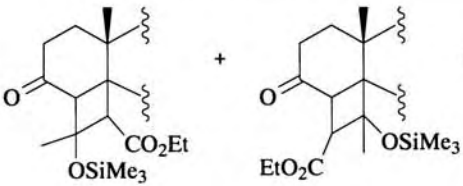
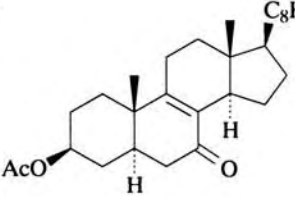
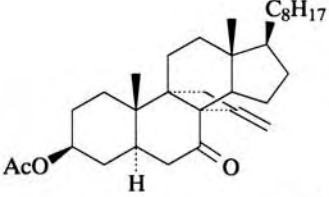
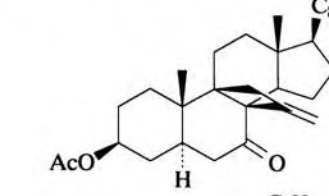
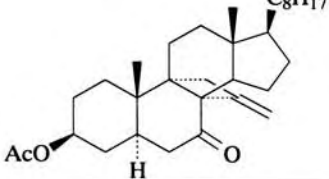
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 24 h		(—) 59
<p>C₂₉</p> 	CH ₂ =C=CH ₂	Silica gel		(—) 291
	CH ₂ =C=CH ₂	Pyrex, C ₆ H ₆ , 1.5 h		(—)
	CH ₂ =C=CH ₂	Pyrex, C ₆ H ₆ , 1.5 h		(72) 208

TABLE VII. BENZOQUINONES AND ALKENES

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—		
<u>R¹ R²</u>	<u>R³ R⁴</u>		I:II:III:IV	
Me H	H OAc		20:80:0:0 (100)	292
Me H	Me OAc		100:0:0:0 (100)	292
Me H	Ph H		55:30:0:15 (100)	293
Me H	Ph Me		(28):(18):(9):(39)	293
Me H	Ph Ph		(25):(0):(48):(0)	293
Me H	<i>p</i> -MeC ₆ H ₄ <i>p</i> -MeC ₆ H ₄		(28):(0):(46):(0)	293
Et H	Ph H		50:26:0:24 (100)	293
Et H	Ph Me		(23):(13):(14):(48)	293
Et H	Ph Ph		(12):(0):(45):(0)	293
Et H	<i>p</i> -MeC ₆ H ₄ <i>p</i> -MeC ₆ H ₄		(13):(0):(44):(0)	293
Me Me	Ph H		(84):(16):(0):(0)	293
Me Me	Ph Me		(38):(20):(0):(0)	293
Me Me	Ph Ph		(87):(0):(0):(0)	293
Et Et	Ph H		(93):(7):(0):(0)	293
Et Et	Ph Me		(77):(13):(0):(0)	293

TABLE VIII. CYCLOHEXADIENES OR CYCLOHEXENEDIONES AND ALKENES

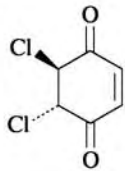
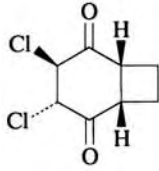

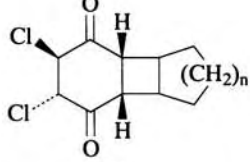


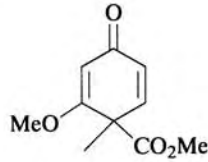

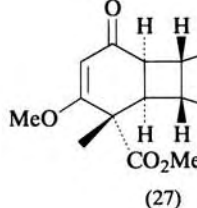
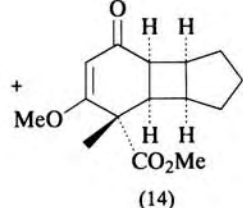
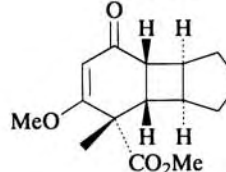
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$CH_2=CH_2$	—	 (57)	294
	 $(CH_2)_n$ $\frac{n}{1}$ $\frac{n}{2}$ $\frac{n}{3}$	$CH_2Cl_2, 0^\circ, 4-5 \text{ h}$	 (50)  (43)  (60)	294
C_{10} 		$THF, 25^\circ, 366 \text{ nm}$	 (27) +  (14) +	295
			 (14)	

TABLE IX. OXAENONES AND ALKENES

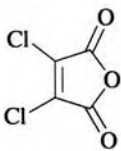

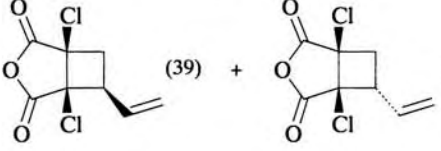
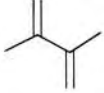
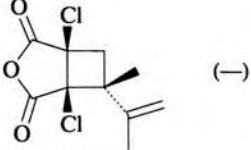
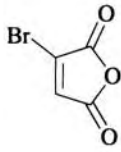
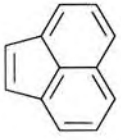
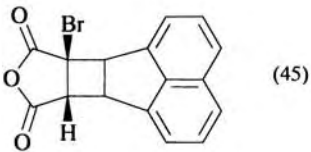
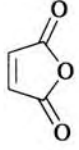

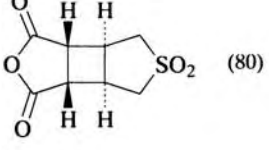

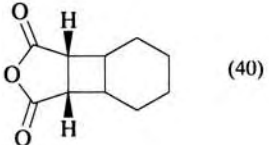
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
^{C₄} 		>300 nm, dioxane, Ph ₂ CO		296
		>300 nm, dioxane, Ph ₂ CO		296
		EtBr		297
		Quartz, CH ₂ Cl ₂ , -78°, 30 h		171, 298
		Pyrex, CH ₃ CN, Ph ₂ CO		299

TABLE IX. OXAENONES AND ALKENES (Continued)

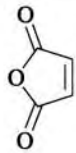
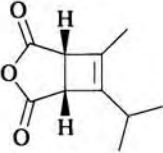
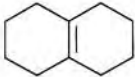
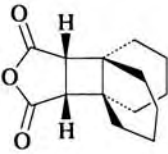
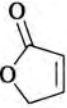
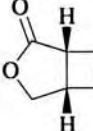
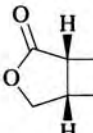
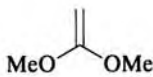
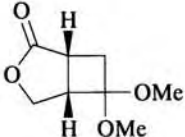
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{C}\equiv\text{CMe}$	Pyrex, CH_3CN , Ph_2CO	 (58)	300
		Pyrex, ether	 (13)	213
	$\text{HC}\equiv\text{CH}$	Acetone, -50° , Vycor	 (54)	301
	$\text{CH}_2=\text{CH}_2$	Acetone, -50° , Vycor	 (44)	301
		Benzene, 254 nm, 19 h	 (62)	301

TABLE IX. OXAENONES AND ALKENES (Continued)


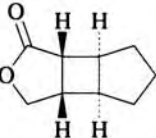

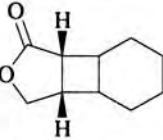
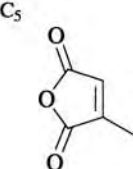
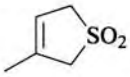
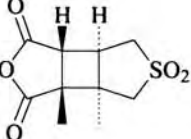
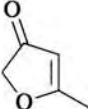
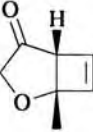
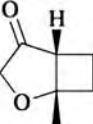
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		CH_3CN , 20 h	 (36)	36
		Ether or acetone	 (72, 42)	67, 301
		Quartz, CH_2Cl_2 , -78° , 30 h	 (80)	298
	$\text{HC}\equiv\text{CH}$	Acetone, -50° , Vycor filter	 (29)	301
	$\text{CH}_2=\text{CH}_2$	Acetone, -50° , Vycor filter	 (44)	301

TABLE IX. OXAENONES AND ALKENES (Continued)

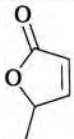
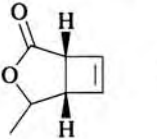
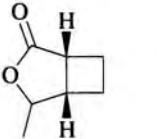

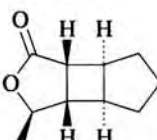
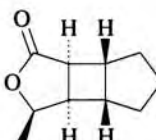
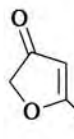
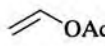
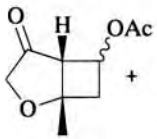
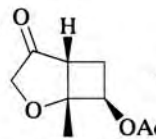
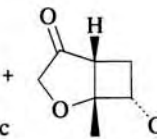
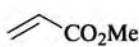
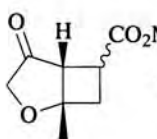
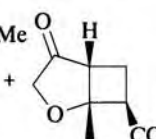
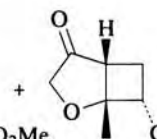
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CH	254 nm	 (14)	301
	CH ₂ =CH ₂	254 nm, acetone, -50°	 (35)	301
		254 nm, CH ₃ CN	 (36) +  (24)	67
		Pyrex, C ₆ H ₆ , 24 h	 +  +  4:7:18 (80)	302
		Pyrex, C ₆ H ₆ , 24 h	 +  +  6:3:1 (65)	302

TABLE IX. OXAENONES AND ALKENES (Continued)

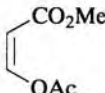
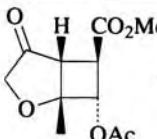
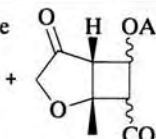
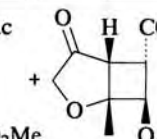
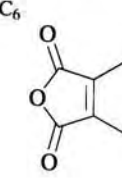

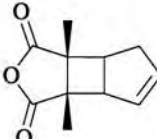

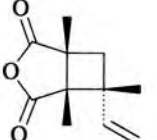
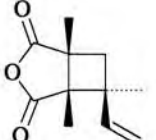
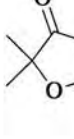

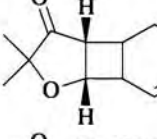
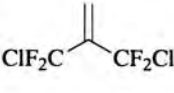
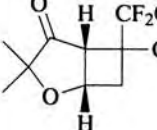
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 24 h	 +  +  12:5:3 (82)	302
		>250 nm, Ph ₂ CO, 115 h	 (9)	296
		>250 nm, C ₆ H ₆ , Ph ₂ CO, 5 d	 (32) +  (26)	296
		>270 nm, Ph ₂ CO, 120 h	 (—)	302
		—	 (—)	45

TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		CH ₃ CN, 15°, 9 h	 +	303
			<u>R</u> CH ₂ OH 56:44 (86) CH ₂ OCH ₂ OCH ₃ 50:50 (80) C(CH ₃) ₂ OH 65:35 (57) CH ₂ OCOPr- <i>i</i> 62:38 (62) CH ₂ OCOBu- <i>t</i> 71:29 (81) CH ₂ OSiMe ₂ Bu- <i>t</i> 68:32 (64) CH ₂ OCPh ₃ 60:40 (29)	
		Pyrex, pentane, 15-18 h	(—)	304
		Pyrex, pentane, 15-18 h	(—)	304

TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, pentane	(95)	304, 46,47
		Pyrex, pentane	(52) + (33) +	204
			(11) + (3)	
		Pyrex, pentane	(60) + (13) +	47, 204
			(13) + (12)	

TABLE IX. OXAENONES AND ALKENES (Continued)


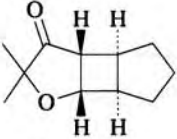
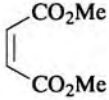
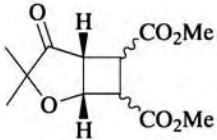

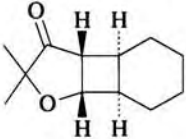

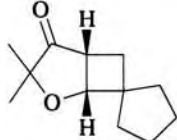

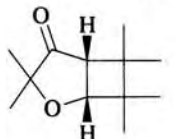
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane	 (89)	46
		—	 5:2:1 (91)	305
		Pyrex, hexane	 (85)	46
		Pyrex, pentane	 (81)	306
		Pyrex, pentane	 (95)	47, 204

TABLE IX. OXAENONES AND ALKENES (Continued)


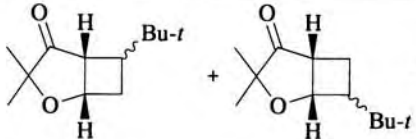
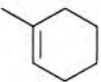
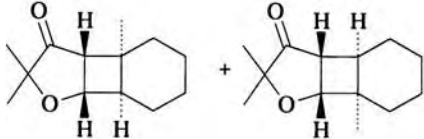
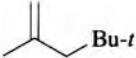
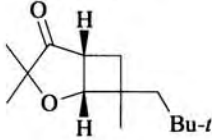
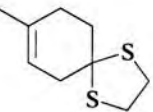
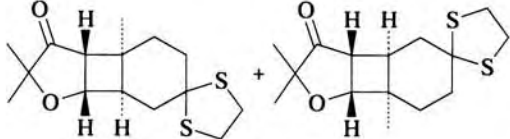
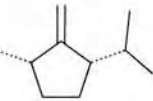
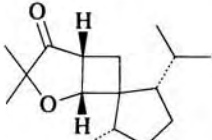
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, pentane	 1:3 (68)	47
		Pyrex, hexane	 1:4 (99)	47
		Pyrex, hexane	 (85)	46
		Pyrex, CH ₂ Cl ₂	 1:3.5 (67)	307
		Pyrex, pentane	 (61)	306

TABLE IX. OXAENONES AND ALKENES (Continued)

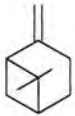
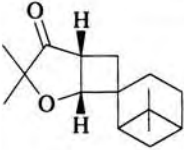
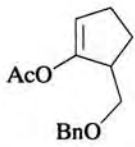
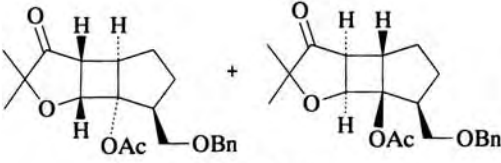
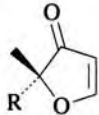

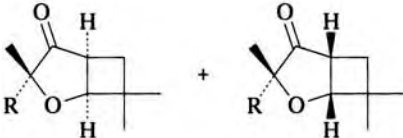
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane	 (91)	46
		Pyrex, hexane	 1:1.8 (70-80)	308
C ₇ 		>280 nm, pentane >280 nm, pentane >280 nm, pentane >350 nm, pentane	 R Et 2.1:1 (94) <i>i</i> -Pr 4.9:1 (97) <i>t</i> -Bu 30:1 (87) C(CH ₃) ₂ OMOM 28:1 (82)	93

TABLE IX. OXAENONES AND ALKENES (Continued)

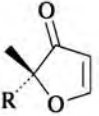

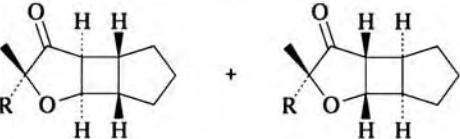
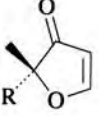

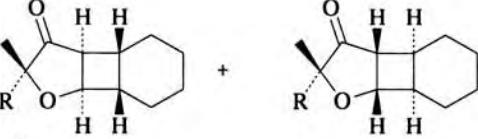
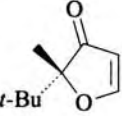

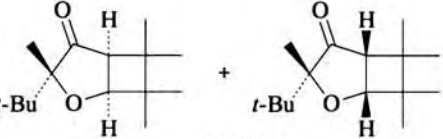
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		>280 nm, pentane >280 nm, pentane >280 nm, pentane >280 nm, pentane >280 nm, pentane >350 nm, pentane	 R Et 1.4:1 (99) <i>i</i> -Pr 40:1 (93) <i>t</i> -Bu 23:1 (95) <i>i</i> -Bu 3.5:1 (99) <i>n</i> -C ₅ H ₁₁ 1.3:1 (97) C(CH ₃) ₂ OMOM 24:1 (82)	93
		>280 nm, pentane >350 nm, pentane	 R <i>t</i> -Bu 25:1 (98) C(CH ₃) ₂ OMOM 25:1 (82)	93
		>280 nm, pentane	 50:1 (97)	93

TABLE IX. OXAENONES AND ALKENES (Continued)

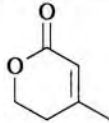
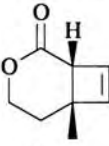
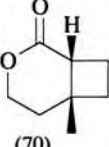
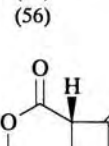
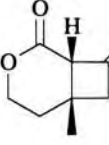
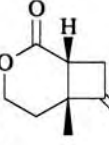
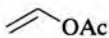
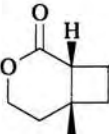
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CH	CH ₃ CN, Vycor or Pyrex	 (73)	310, 309
	CH ₂ =CH ₂	Vycor, acetone Quartz, C ₆ H ₆ , PhCOCH ₃	 (70)  (56)	301, 311, 312
	CH ₂ =C=CH ₂	Vycor, acetone, -78°, 4 h Acetone, 25° CH ₂ Cl ₂ , xanthone, -78° CH ₃ OH, acetone, -78° Dichloroethane, acetone, -78° CH ₂ Cl ₂ , acetone, -35°	 +  3:2 (80) 5:3 (82) 4:3 (60) 2:3 (27) 3:2 (100) 3:2 (74)	312
	 OAc	—	 (4)	312

TABLE IX. OXAENONES AND ALKENES (Continued)

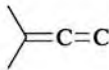
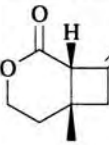
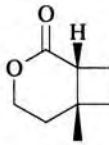
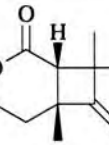
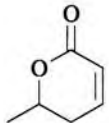
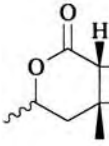
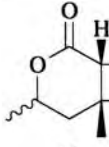
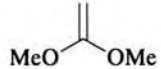
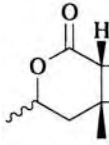
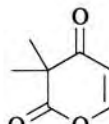
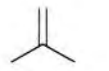
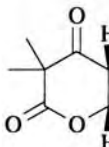
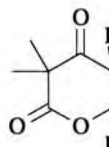
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	 C=CH ₂	0°	 +  +  18:26:56 (53)	312
	HC≡CH	Acetone	 (66)	301
	CH ₂ =CH ₂	Acetone	 (70)	301
	 OMe	Ether	 (—)	301
		—	 +  (—)	270

TABLE IX. OXAENONES AND ALKENES (Continued)

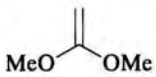
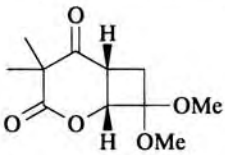
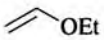
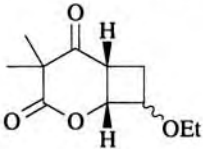

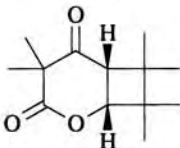
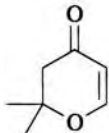
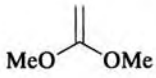
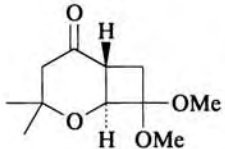
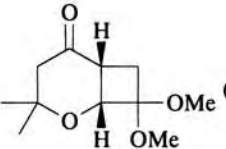

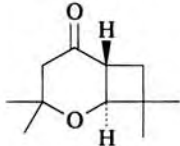
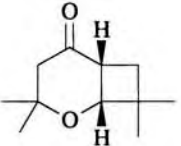
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (—)	270
		—	 (—)	270
		—	 (—)	313
		—	 +  (—)	313
		—	 +  (—)	313

TABLE IX. OXAENONES AND ALKENES (Continued)


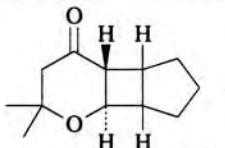
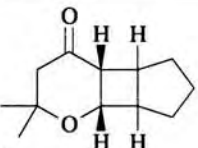

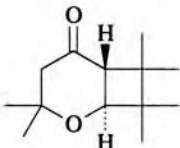
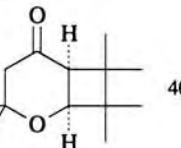
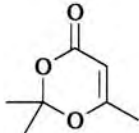

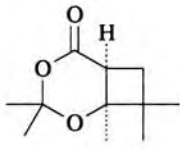
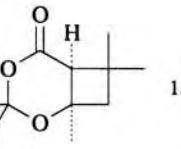

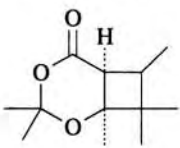
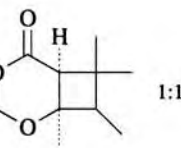

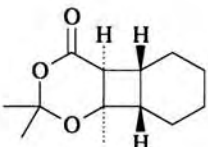
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		>340 nm	 +  1:8 (—)	313
		>340 nm	 +  40:60 (—)	313
		Corex, hexane, 24 h	 +  1.6:1 (93)	48
		Corex, hexane, 24 h	 +  1:19 (100)	48
		Corex, hexane, 24 h	 (98)	48

TABLE IX. OXAENONES AND ALKENES (Continued)


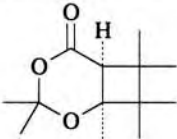
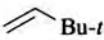
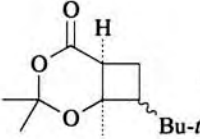
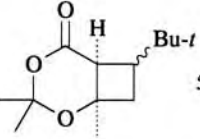

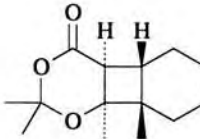
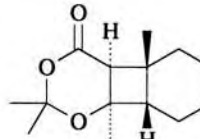

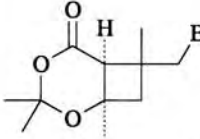
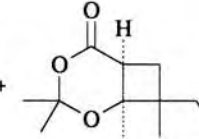
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, hexane, 24 h	 (90)	48
		Corex, hexane, 24 h	 +  5:1 (82)	48
		Corex, hexane, 24 h	 +  1:8 (86)	48
		Corex, hexane, 24 h	 +  19:1 (88)	48

TABLE IX. OXAENONES AND ALKENES (Continued)

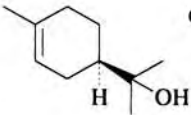
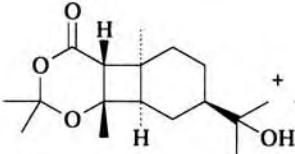
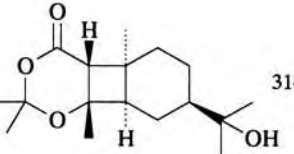
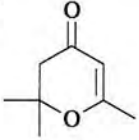

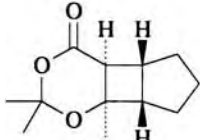

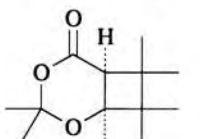
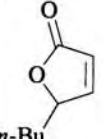
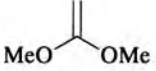
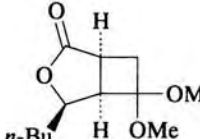
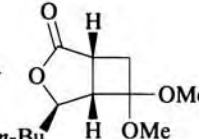
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, acetone:CH ₃ CN 1:9, 20 h	 +  1:3.35 (88)	314
		>340 nm	 (—)	313
		>340 nm	 (—)	313
		C ₆ H ₆	 +  (—)	301

TABLE IX. OXAENONES AND ALKENES (Continued)

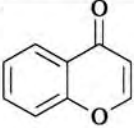
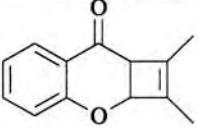
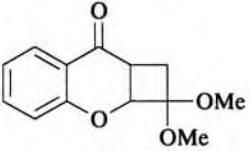

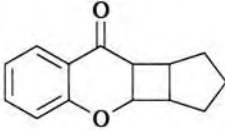

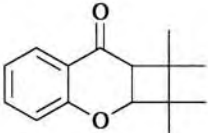
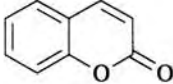
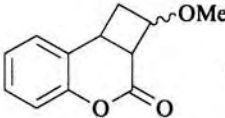
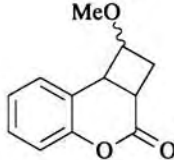
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	MeC≡CMe	Pyrex	 (—)	315
	MeO-C(=C)-OMe	Pyrex	 (—)	315
		Pyrex	 (—)	315
		Pyrex	 (—)	315
	CH ₂ =CH-OMe	—	 +  (—)	316

TABLE IX. OXAENONES AND ALKENES (Continued)


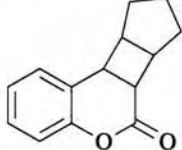
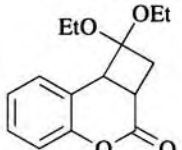

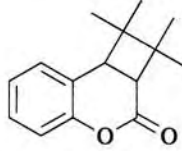
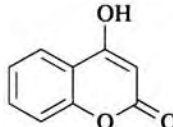
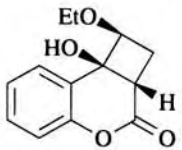
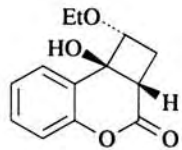
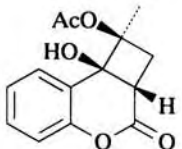
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, dioxane, Ph ₂ CO	 (50)	317, 318
	EtO-C(=C)-OEt	—	 (41)	317, 319
		Pyrex, dioxane, Ph ₂ CO EtOAc, >310 nm, 68 h	 (51) (15)	319 317
	CH ₂ =CH-OEt	—	 (16) +  (10)	320
	CH ₃ -C(=C)-OAc	—	 (75)	320

TABLE IX. OXAENONES AND ALKENES (Continued)


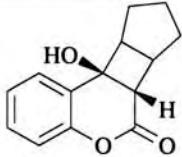
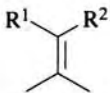
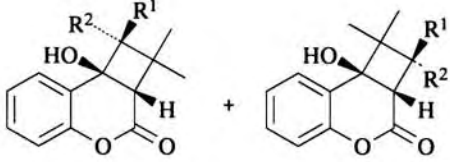

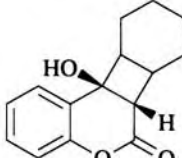

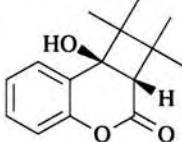
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, <i>t</i> -BuOH	 (51)	320, 321
		—	 + R ¹ = H, R ² = Me (11) R ¹ = Me, R ² = H (16) R ¹ = Me, R ² = H (22) R ¹ = H, R ² = Me (32)	320
		Pyrex, <i>t</i> -BuOH	 (67)	320, 321
		Pyrex, <i>t</i> -BuOH	 (75)	320, 321

TABLE IX. OXAENONES AND ALKENES (Continued)


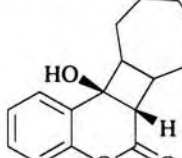

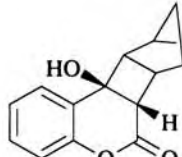

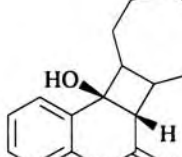
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, <i>t</i> -BuOH	 (55)	321
		Pyrex, <i>t</i> -BuOH	 (30)	321
		Pyrex, <i>t</i> -BuOH	 (58)	320, 321

TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 3.1:1 + 303	
C ₁₀			 1:1 + 303 (64)	
	CH ₂ =CH ₂	Vycor, 25°	 (49)	301
	CH ₂ =CH ₂	Pyrex, 25°	 (52)	301
		—	 (37)	301

TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CH	Acetone, >295 nm, Pyrex, -20°	 (50)	322
		>340 nm	 (—)	313
C ₁₂			 (10)	323
		350 nm, CH ₃ OH	 (4)	323
		350 nm, CH ₃ OH	 (—)	323

TABLE IX. OXAENONES AND ALKENES (Continued)

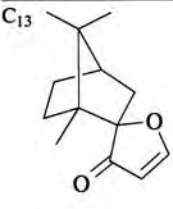

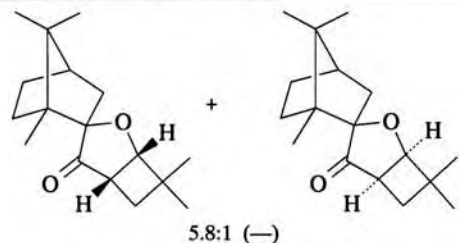

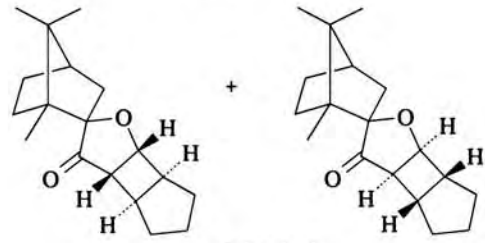

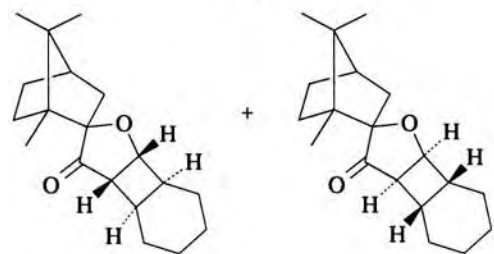
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 		Pyrex, hexane	 5.8:1 (—)	324
		Pyrex, hexane	 6.1:1 (—)	324
		Pyrex, hexane	 7.7:1 (—)	324

TABLE IX. OXAENONES AND ALKENES (Continued)

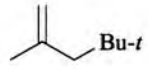
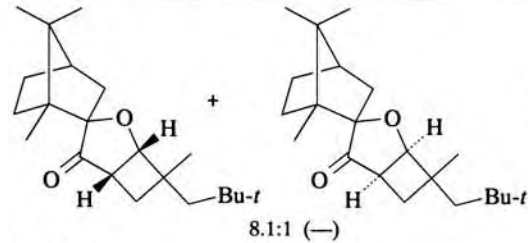
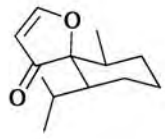

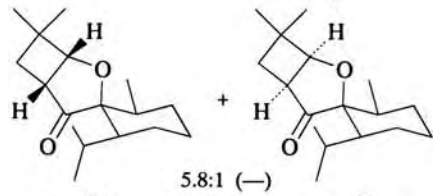

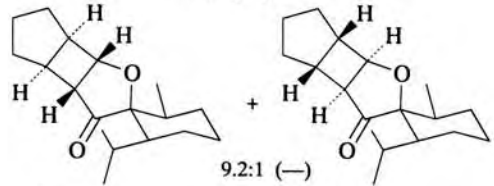

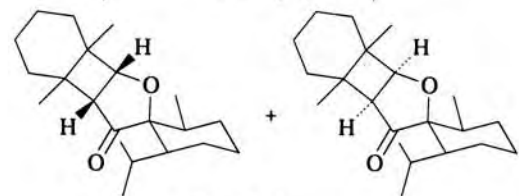
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane	 8.1:1 (—)	324
		Pyrex, hexane	 5.8:1 (—)	324
		Pyrex, hexane	 9.2:1 (—)	324
		Pyrex, hexane	 8.7:1 (—)	324

TABLE IX. OXAENONES AND ALKENES (Continued)

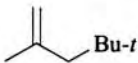
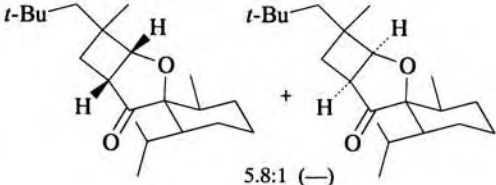
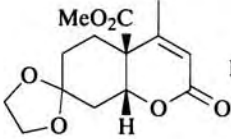
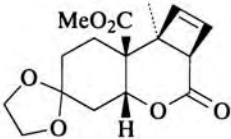
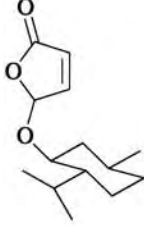
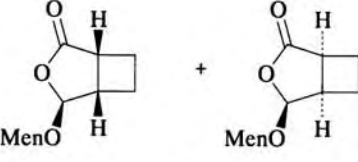
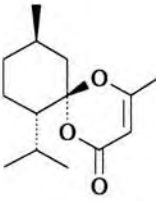

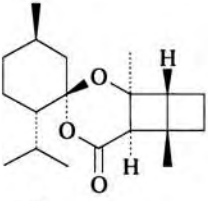


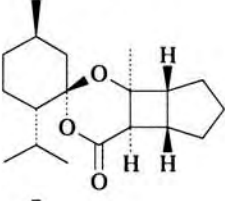
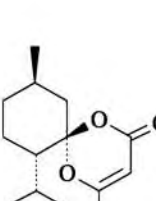
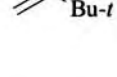
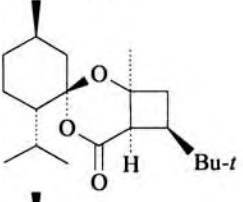
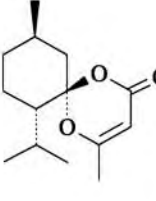

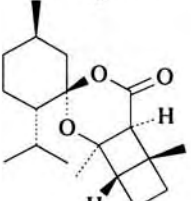
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane	 5.8:1 (—)	324
C ₁₄ 	HC≡CH	Pyrex, CH ₃ CN	 (—)	309
	CH ₂ =CH ₂	-85° -75° -55° 14°	 73:27 (75) 73:27 (85) 71:29 (98) 70:30 (98)	95

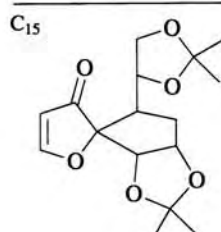

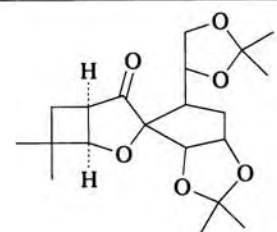

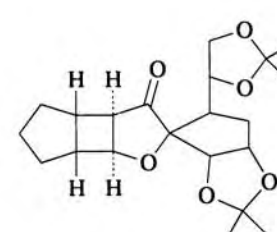
TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (43)	96
		—	 (25)	96
		—	 (60)	96
		—	 (44)	96

450



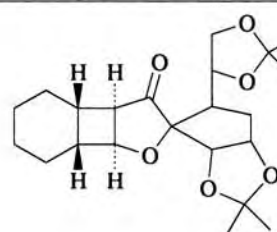
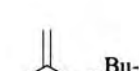
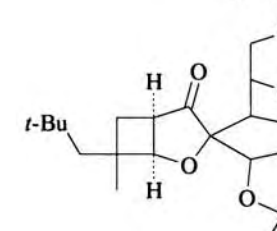
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TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₅		Pyrex, hexane	 + 3.8:1 (—)	324
		Pyrex, hexane	 + 5.7:1 (—)	324

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TABLE IX. OXAENONES AND ALKENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, hexane	 + 4.8:1 (—)	324
		Pyrex, hexane	 + 7.2:1 (—)	324

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TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES

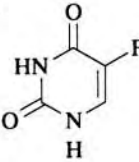
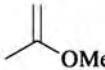
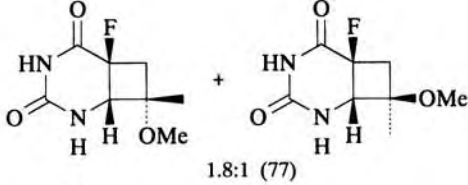

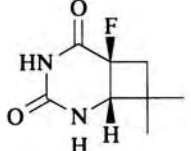
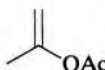
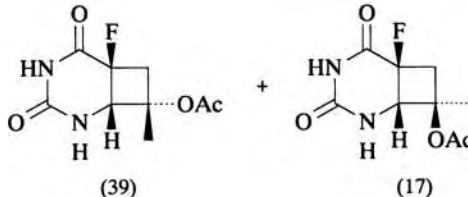
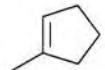
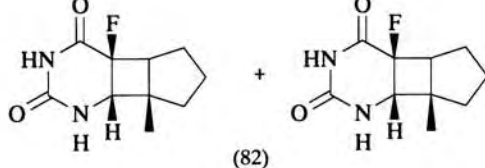
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, acetone, 2.5 h		325
		Corex, acetone, 4.5 h		326, 327
		Corex, acetone, 4.5 h		163
		Corex, acetone, 4.5 h		163, 326

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

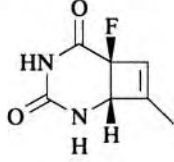

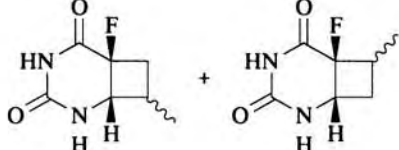
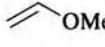
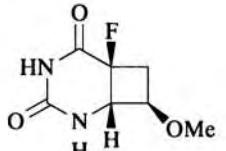
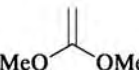
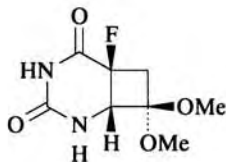
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CMe	Corex, acetone:H ₂ O 4:1, 1.5 h		49
		Corex, acetone, 4.5 h		163, 326
		Corex, acetone, 4.5 h		325
		Corex, acetone, 4.5 h		325

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)


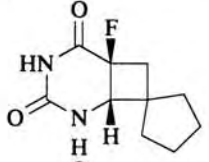

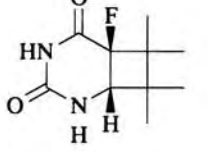
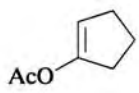
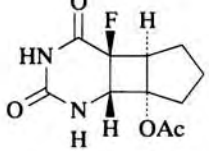
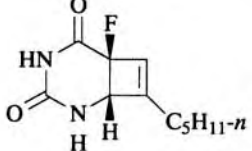
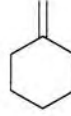
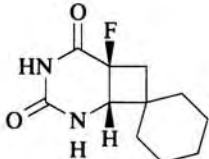
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, acetone, 4.5 h	 (76)	163, 326
		Corex, acetone, 4.5 h	 (79)	163, 326
		Corex, acetone, 4.5 h	 (64)	163, 326
	$\text{HC}\equiv\text{CC}_5\text{H}_{11-n}$	Corex, acetone, 4.5 h	 (29)	49
		Corex, acetone, 4.5 h	 (72)	163, 326

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

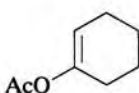
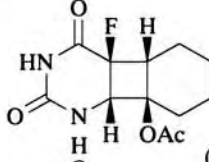
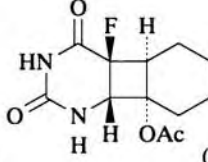
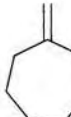
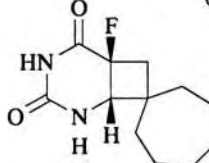
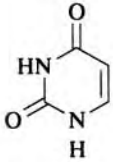
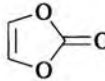
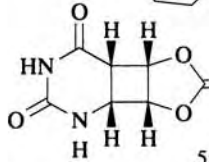
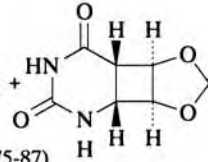
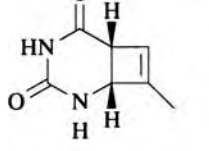
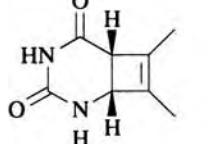
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (14) +  (85)	163
		Corex, acetone, 4.5 h	 (78)	163, 326
		260 nm, H ₂ O, acetone, 14-16 h	 +  5:2 (75-87)	328
	$\text{HC}\equiv\text{CMe}$	Corex, acetone, H ₂ O, 1.5 h	 (43)	49
	$\text{MeC}\equiv\text{CMe}$	Corex, acetone, H ₂ O, 1.5 h	 (54)	49

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.												
		Corex, acetone, 4.5 h		3.4:1 (92) 326												
	$R^1C\equiv CR^2$	Corex, acetone, H ₂ O, 1.5 h	 <table border="1"> <tr> <td>R¹</td> <td>R²</td> <td></td> </tr> <tr> <td>H</td> <td>Pr</td> <td>(30)</td> </tr> <tr> <td>Et</td> <td>Et</td> <td>(31)</td> </tr> <tr> <td>H</td> <td>C₃H₁₁</td> <td>(31)</td> </tr> </table>	R ¹	R ²		H	Pr	(30)	Et	Et	(31)	H	C ₃ H ₁₁	(31)	49
R ¹	R ²															
H	Pr	(30)														
Et	Et	(31)														
H	C ₃ H ₁₁	(31)														
C ₅ 	MeC≡CMe	—		(32) 49												
		—		3.4:1 (92) 326												

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.												
		Corex, acetone, 4.5 h		2.9:1 (97) 326												
		—		50:1 (—) 329												
		Corex, acetone	 (16) (32)	163												
C ₆ 		313 nm, dioxane, 24 h	 <table border="1"> <tr> <td>X</td> <td>R</td> <td></td> </tr> <tr> <td>Cl</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Br</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>I</td> <td>H</td> <td>(—)</td> </tr> </table>	X	R		Cl	H	(—)	Br	H	(—)	I	H	(—)	330
X	R															
Cl	H	(—)														
Br	H	(—)														
I	H	(—)														

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		CH ₃ CN, acetone		331
		—		2:1 (63-100) 329
		313 nm, dioxane, 24 h		330
			X R Cl Me (—) Br Me (—)	
		—		331

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		CH ₃ CN, acetone		1:1 (70) 331
		Acetone, -78°, 40 h Corex, CH ₃ CN, acetone, 40 h CH ₃ CN, acetone Acetone, -78°, 23 h CH ₃ CN, acetone, 4.5 h		332
			R ¹ R ² H H (91) H OAc (96) H OEt (51) Me Me (94) Me OAc (65)	
		CH ₃ CN, acetone, 6 h		332
		CH ₃ CN, acetone, 12 h		332

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

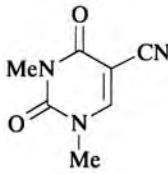

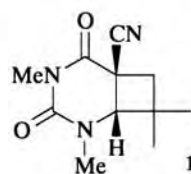
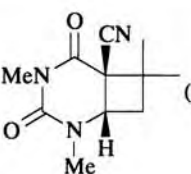
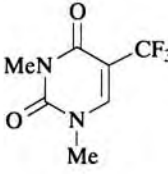

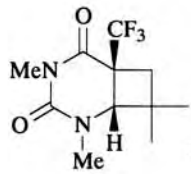
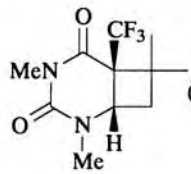
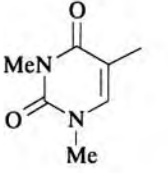

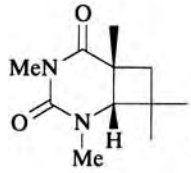
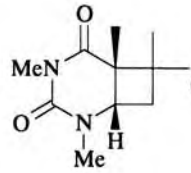
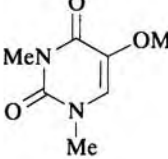

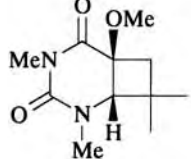
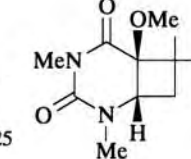
Enone	Alkene	Reaction Conditions	Product(s) and Yield d(s) (%)	Refs.
C ₇ 		—	 +  (63-100) 1:1	329
		—	 +  (63-100) 32:1	329
		—	 +  (63-100) 1.5:1	329
		—	 +  (—) 1:25	329

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

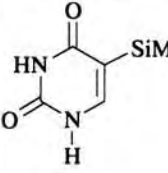
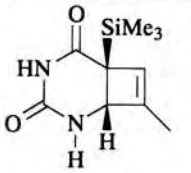

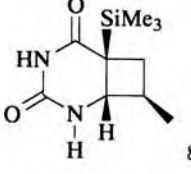
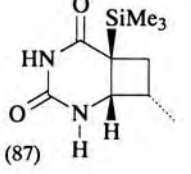

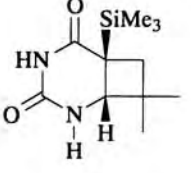

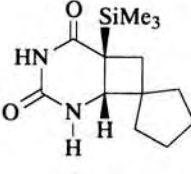
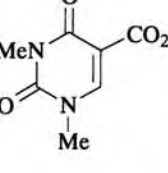

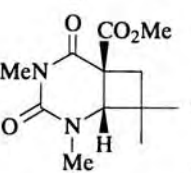
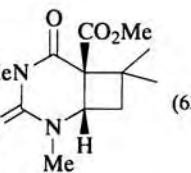
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 	HC≡CMe	Acetone, 2 h	 (68)	169
		Acetone, 3 h	 +  85:15 (87)	169
		Acetone, 3 h	 (90)	169
		Acetone, 1.5 h	 (85)	169
C ₈ 		—	 +  (63-100) 4:1	329

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)

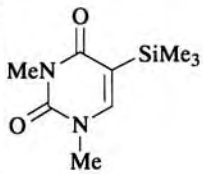

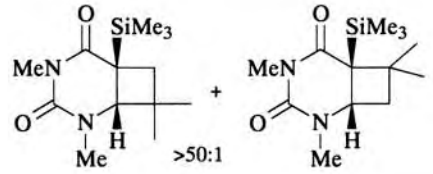
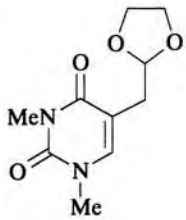

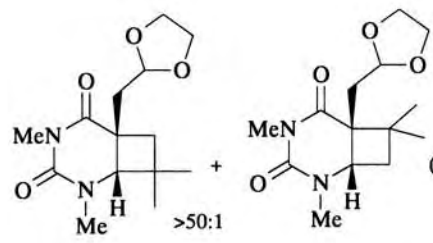
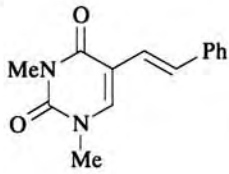
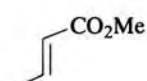
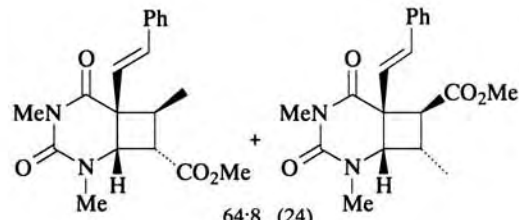
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 		—	 (—)	329
C ₁₀ 		—	 (63-100)	329
C ₁₄ 		350 nm, CH ₂ Cl ₂	 333	333

TABLE X. PYRIMIDINES AND ALKENES OR ACETYLENES (Continued)


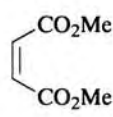
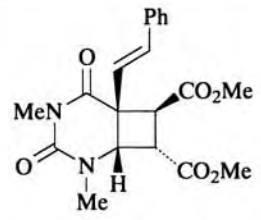


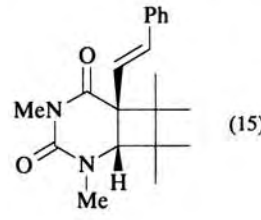

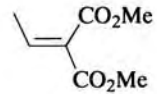
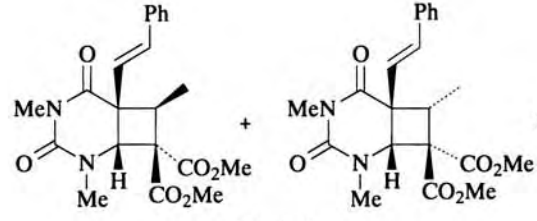
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, CH ₂ Cl ₂	 (—)	333
		350 nm, CH ₂ Cl ₂	 (15)	333
		350 nm, CH ₂ Cl ₂	 333	333

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES

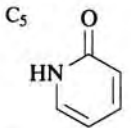
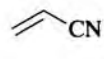
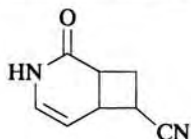
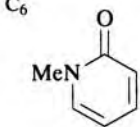
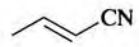
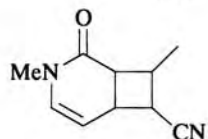
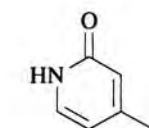
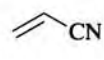
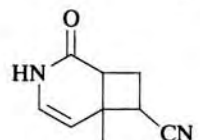
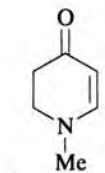
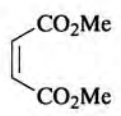
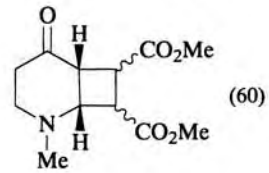
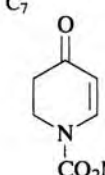
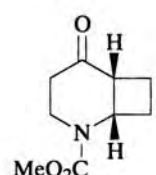
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₅ 		Pyrex, EtOH, 30 h	 (41)	184
C ₆ 		Pyrex, EtOH, 30 h	 (26)	184
		Pyrex, EtOH, 30 h	 (25)	184
		Pyrex, acetone, 3 h	 (60)	334
C ₇ 	CH ₂ =CH ₂	-70°, 1.5 h	 (93)	335

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)


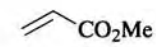
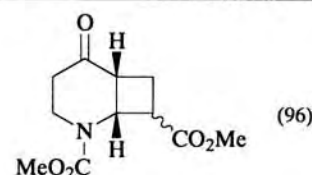

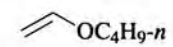
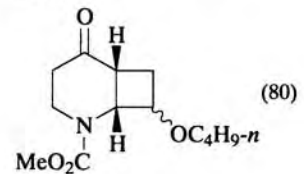

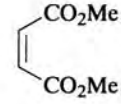
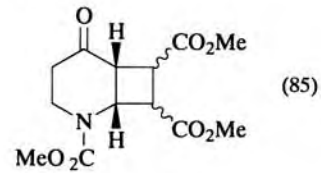

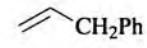
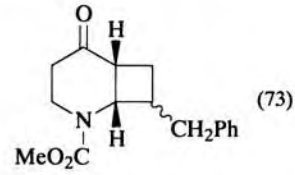


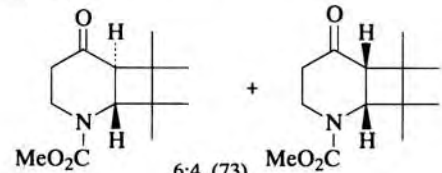
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		-70°, 1.5 h	 (96)	335
		-70°, 1.5 h	 (80)	335
		-70°, 1.5 h	 (85)	335
		-70°, 1.5 h	 (73)	335
		-70°, 1.5 h	 (73) 6:4	335

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

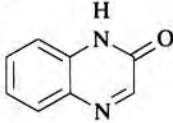

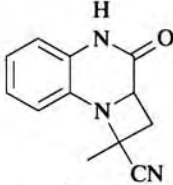
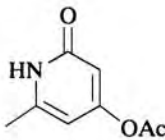
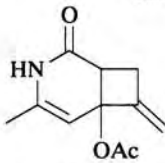
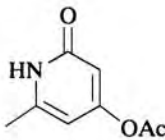
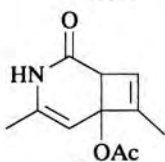
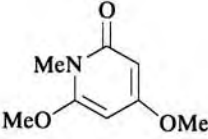

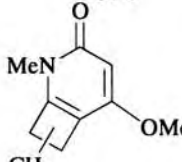
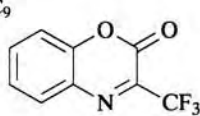
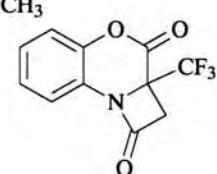
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, benzene	 (41)	336
	$\text{CH}_2=\text{C}=\text{CH}_2$	350 nm, acetone	 (—)	337
	$\text{CH}_2=\text{C}=\text{CH}_2$	350 nm, acetone	 (62)	337
		350 nm, acetone	 (75)	338
	$\text{CH}_2=\text{C}=\text{O}$	>300 nm, C_6H_6	 (61)	337

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

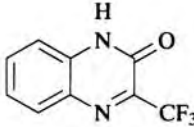
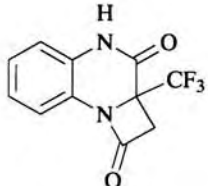
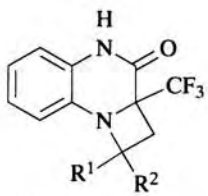
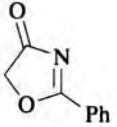
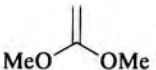
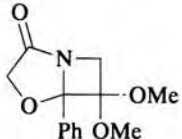
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	$\text{CH}_2=\text{C}=\text{O}$	>300 nm, C_6H_6	 (82)	337
	$\text{R}^1\text{C}=\text{C}\text{R}^2$	>300 nm, C_6H_6		
		>300 nm, C_6H_6	R^1 H, R^2 H (17)	339
		>300 nm, C_6H_6	R^1 H, R^2 OEt (—)	339
		>300 nm, C_6H_6	R^1 Me, R^2 Me (75)	339
		>300 nm, C_6H_6	R^1 Me, R^2 CO_2Me (100)	339
		>300 nm, MeOH	R^1 H, R^2 $\text{CO}_2\text{CH}=\text{CH}_2$ (75)	339
		Corex, C_6H_6 , 8 h	 (65)	340

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

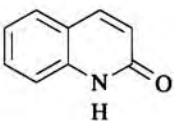
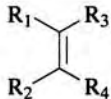
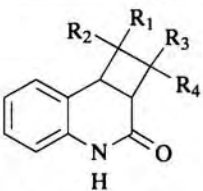

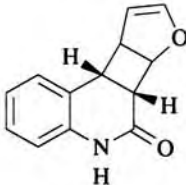
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
			 + dimers	
		MeCONMe ₂ , 24 h , 5 d	R ¹ Cl R ² H R ³ Cl R ⁴ Cl (20)	341
		EtOH, 96 h	R ¹ Cl R ² H R ³ Cl R ⁴ H (80)	342
		EtOH, 144 h	R ¹ CN R ² H R ³ H R ⁴ H (63)	341
		EtOH, 72 h	R ¹ MeO R ² H R ³ H R ⁴ H (65)	341,316
		MeCONMe ₂ , 24 h	R ¹ AcO R ² H R ³ H R ⁴ H (8)	341
		EtOH, 72 h	R ¹ MeO R ² H R ³ MeO R ⁴ H (100)	341
		EtOH, 72 h	R ¹ Me R ² H R ³ Me R ⁴ H (50)	341,342
		EtOH, Pyrex	R ¹ —(CH ₂) ₃ — R ² H R ³ H R ⁴ H (54)	341
		EtOH, 20 h	R ¹ —(CH ₂) ₄ — R ² H R ³ H R ⁴ H (94)	343
		EtOH, 72 h	R ¹ Me R ² Me R ³ Me R ⁴ Me (90)	341
		EtOH, 48 h	R ¹ Et R ² H R ³ Et R ⁴ H (50)	341
		EtOH, 144 h	R ¹ OC ₄ H ₉ R ² H R ³ H R ⁴ H (79)	341
		EtOH, 192 h	R ¹ —(CH ₂) ₆ — R ² H R ³ H R ⁴ H (49)	341
		EtOH, 10 h	R ¹ Ph R ² H R ³ Ph R ⁴ H (20)	341
			R ¹ —O(CH ₂) ₂ — R ² H R ³ H R ⁴ H (—)	209
		Pyrex, EtOH, 10 h	 (47)	209

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

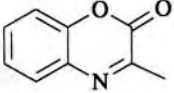
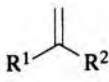
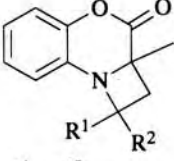
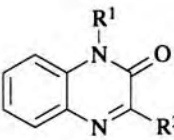
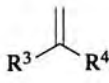
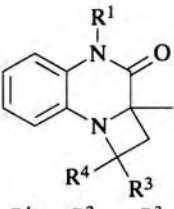
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, C ₆ H ₆ , 25°		344
			R ¹ H R ² CN (65)	
			R ¹ Me R ² CN (85)	
			R ¹ H R ² CO ₂ Me (41)	
			R ¹ H R ² CO ₂ CH=CH ₂ (20)	
			R ¹ Me R ² CO ₂ Me (58)	
			R ¹ H R ² Ph (47)	
			R ¹ Me R ² Ph (40)	
			R ¹ Ph R ² Ph (50)	
		Pyrex, benzene		336
			R ¹ Me R ² H R ³ H R ⁴ CN (29,33)	
			R ¹ Me R ² H R ³ Me R ⁴ CN (91)	
			R ¹ H R ² Me R ³ Me R ⁴ CN (99)	
			R ¹ H R ² Me R ³ Me R ⁴ CO ₂ Me (58,40)	
			R ¹ Me R ² H R ³ H R ⁴ Ph (52)	
			R ¹ H R ² Me R ³ H R ⁴ CO ₂ CH=CH ₂ (50)	

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																
		—	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>CN</td> <td>(31)</td> </tr> <tr> <td>CN</td> <td>H</td> <td>CN</td> <td>(25)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>CN</td> <td>(52)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>CO₂Me</td> <td>(37)</td> </tr> <tr> <td>CO₂Me</td> <td>H</td> <td>CO₂Me</td> <td>(29)</td> </tr> <tr> <td>Ph</td> <td>H</td> <td>CN</td> <td>(95)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Ph</td> <td>(72)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		H	H	CN	(31)	CN	H	CN	(25)	H	Me	CN	(52)	H	Me	CO ₂ Me	(37)	CO ₂ Me	H	CO ₂ Me	(29)	Ph	H	CN	(95)	H	Ph	Ph	(72)	345
R ¹	R ²	R ³																																		
H	H	CN	(31)																																	
CN	H	CN	(25)																																	
H	Me	CN	(52)																																	
H	Me	CO ₂ Me	(37)																																	
CO ₂ Me	H	CO ₂ Me	(29)																																	
Ph	H	CN	(95)																																	
H	Ph	Ph	(72)																																	
		350 nm, CH ₃ CN, 16 h		305																																
		350 nm, CH ₃ CN		305																																

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		350 nm, CH ₃ CN, 16 h		305
		350 nm, CH ₃ CN		305
		350 nm, CH ₃ CN		305
		Pyrex, EtOH		347

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

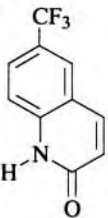
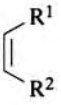
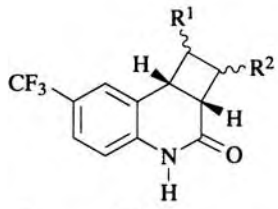

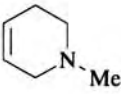
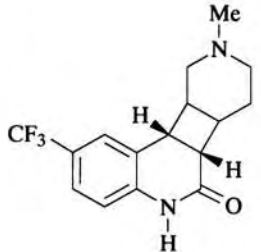
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																		
		C ₆ H ₆ , acetone Dioxane, acetone Dichloroethane, acetone Dioxane, acetone Dioxane, acetone		346																		
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(12)</td> </tr> <tr> <td>H</td> <td>CO₂H</td> <td>(50)</td> </tr> <tr> <td>H</td> <td>CO₂Et</td> <td>(70)</td> </tr> <tr> <td>—(CH₂)₃—</td> <td></td> <td>(35)</td> </tr> <tr> <td>CO₂Et</td> <td>CO₂Et</td> <td>(53)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	H	(12)	H	CO ₂ H	(50)	H	CO ₂ Et	(70)	—(CH ₂) ₃ —		(35)	CO ₂ Et	CO ₂ Et	(53)	
			R ¹	R ²	Yield (%)																	
			H	H	(12)																	
			H	CO ₂ H	(50)																	
H	CO ₂ Et	(70)																				
—(CH ₂) ₃ —		(35)																				
CO ₂ Et	CO ₂ Et	(53)																				
		Dioxane, acetone		(50) 346																		

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

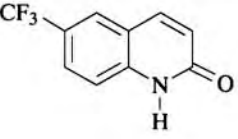

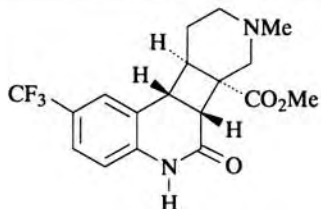
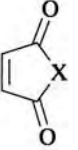
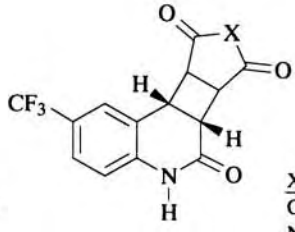
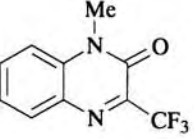
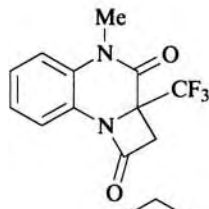
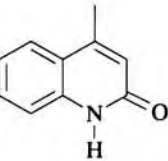

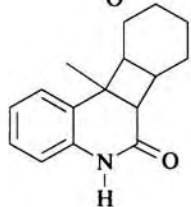
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Dioxane, acetone		(66) 346
		Dichloroethane, Ph ₂ CO C ₆ H ₆ , Ph ₂ CO		(14) (10) 346
	CH ₂ =C=O	>300 nm, C ₆ H ₆		(61) 337
		Pyrex, MeOH, 9 h		(100) 343

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

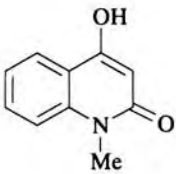

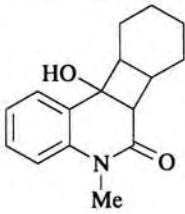
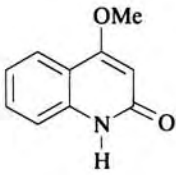

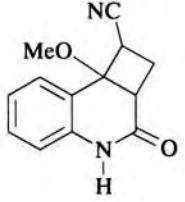
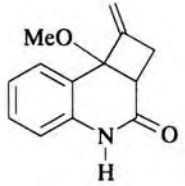
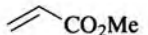
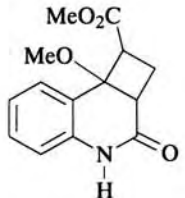
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (34)	348
		MeOH	 (—)	337
	$\text{CH}_2=\text{C}=\text{CH}_2$	—	 (77)	349
		—	 (—)	337

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

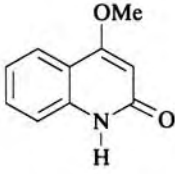

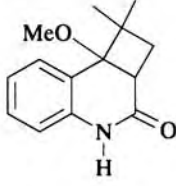

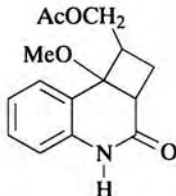
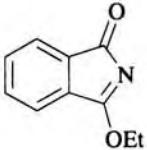

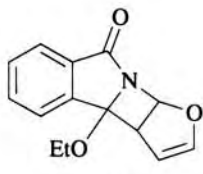
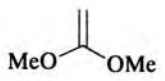
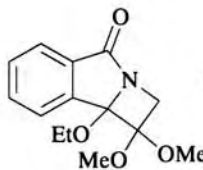
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		—	 (80)	337
		—	 (—)	337
		—	 (54)	350
		Pyrex, <i>t</i> -BuOH, 15 min	 (50)	350, 351

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)


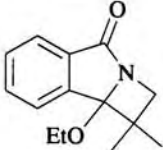

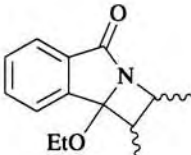

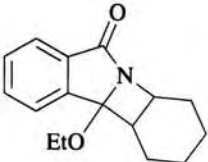

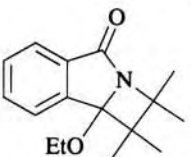
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, CH ₂ Cl ₂ , -12°	 (23)	350
		Pyrex, -15°	 (62)	350
		Pyrex, CH ₂ Cl ₂	 (51)	350 351
		CH ₂ Cl ₂	 (20)	350

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

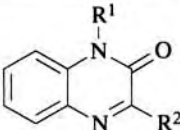
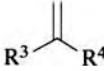
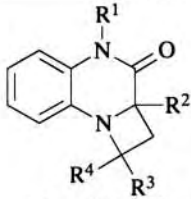
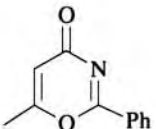
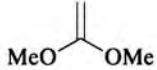
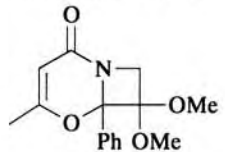
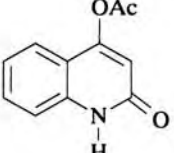

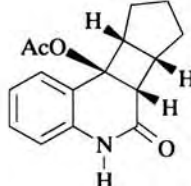
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																																																						
		Pyrex, benzene	 <table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th></th> </tr> </thead> <tbody> <tr><td>Me</td><td>Me</td><td>H</td><td>CN</td><td>(96)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>CO₂Me</td><td>(40)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>CO₂CH=CH₂</td><td>(32)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>2-C₅H₄N</td><td>(69)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>4-C₅H₄N</td><td>(86)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td>Ph</td><td>(63)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td><i>p</i>-ClC₆H₄</td><td>(40)</td></tr> <tr><td>Me</td><td>Me</td><td>H</td><td><i>p</i>-MeC₆H₄</td><td>(46)</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>CN</td><td>(94)</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Me</td><td>(13)</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>CO₂Me</td><td>(45,39)</td></tr> <tr><td>Me</td><td>Me</td><td>Me</td><td>Ph</td><td>(22)</td></tr> <tr><td>Me</td><td>Me</td><td>Ph</td><td>Ph</td><td>(24)</td></tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴		Me	Me	H	CN	(96)	Me	Me	H	CO ₂ Me	(40)	Me	Me	H	CO ₂ CH=CH ₂	(32)	Me	Me	H	2-C ₅ H ₄ N	(69)	Me	Me	H	4-C ₅ H ₄ N	(86)	Me	Me	H	Ph	(63)	Me	Me	H	<i>p</i> -ClC ₆ H ₄	(40)	Me	Me	H	<i>p</i> -MeC ₆ H ₄	(46)	Me	Me	Me	CN	(94)	Me	Me	Me	Me	(13)	Me	Me	Me	CO ₂ Me	(45,39)	Me	Me	Me	Ph	(22)	Me	Me	Ph	Ph	(24)	336
R ¹	R ²	R ³	R ⁴																																																																							
Me	Me	H	CN	(96)																																																																						
Me	Me	H	CO ₂ Me	(40)																																																																						
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Me	Me	Me	CO ₂ Me	(45,39)																																																																						
Me	Me	Me	Ph	(22)																																																																						
Me	Me	Ph	Ph	(24)																																																																						
		Pyrex, CH ₂ Cl ₂ , 2 h	 (78)	352																																																																						
		Pyrex, MeOH, 12 h	 (64)	348																																																																						

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

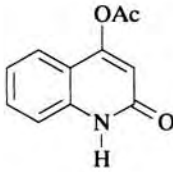

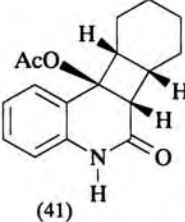
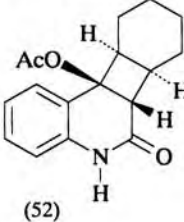

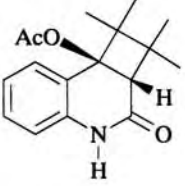
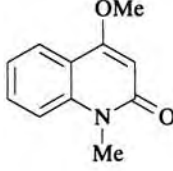
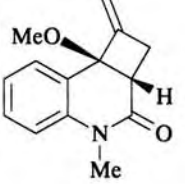
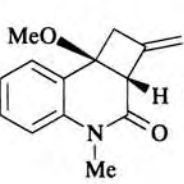

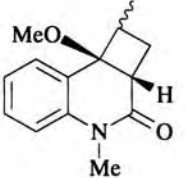
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, MeOH, 12 h	 (41) +  (52)	348
		Pyrex, MeOH	 (11)	348
	CH ₂ =C=CH ₂	MeOH	 (60) +  (10)	337
		—	 (—)	337

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

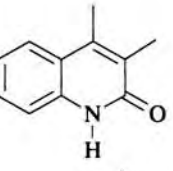

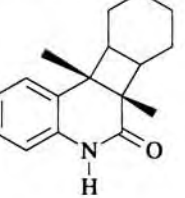
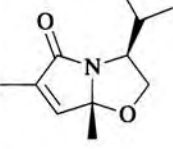
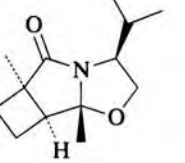
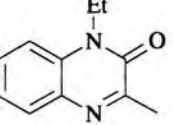
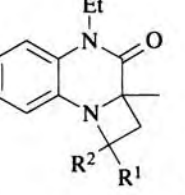
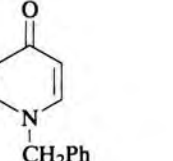
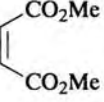
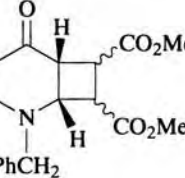
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.												
		Pyrex, MeOH, 10 h	 (63)	343												
	CH ₂ =CH ₂	CH ₂ Cl ₂ , acetophenone, 5 h, -78°	 (93)	94												
	R ¹ —C=C—R ²	Pyrex, benzene		336												
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield(s) (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CN</td> <td>(100)</td> </tr> <tr> <td>Ph</td> <td>CO₂Me</td> <td>(57, 39)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(14)</td> </tr> </tbody> </table>	R ¹	R ²	Yield(s) (%)	Me	CN	(100)	Ph	CO ₂ Me	(57, 39)	Me	Ph	(14)	
R ¹	R ²	Yield(s) (%)														
Me	CN	(100)														
Ph	CO ₂ Me	(57, 39)														
Me	Ph	(14)														
		Acetone, 4 h	 (66)	334												

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

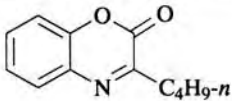
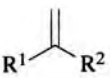
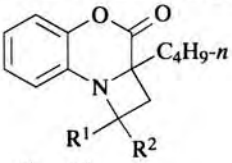
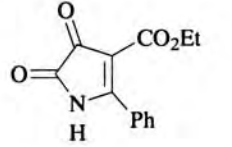
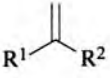
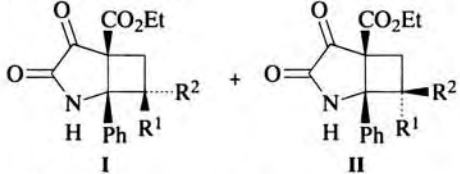
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																																												
		Pyrex, C ₆ H ₆ , 25°	 <table border="1" data-bbox="979 408 1284 516"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CN</td> <td>(75)</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>(59)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(42)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Me	CN	(75)	Me	CO ₂ Me	(59)	Ph	Ph	(42)	344																																																
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Me	CN	(75)																																																														
Me	CO ₂ Me	(59)																																																														
Ph	Ph	(42)																																																														
		Dimethoxyethane, >300 nm	 <table border="1" data-bbox="979 688 1354 1099"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>I (%)</th> <th>II (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>CH=CH₂</td> <td>(48)</td> <td>(20)</td> </tr> <tr> <td>H</td> <td>OAc</td> <td>(6)</td> <td>(63)</td> </tr> <tr> <td>H</td> <td>Et</td> <td>(27)</td> <td>(3)</td> </tr> <tr> <td>H</td> <td>OEt</td> <td>(6)</td> <td>(62)</td> </tr> <tr> <td>H</td> <td>CH=CHMe (Z)</td> <td>(35)</td> <td>(20)</td> </tr> <tr> <td>H</td> <td>CH=CHMe (E)</td> <td>(27)</td> <td>(18)</td> </tr> <tr> <td>Me</td> <td>CH=CH₂</td> <td>(60)</td> <td>(—)</td> </tr> <tr> <td>Me</td> <td>OAc</td> <td>(6)</td> <td>(36)</td> </tr> <tr> <td>H</td> <td>OC₄H_{9-i}</td> <td>(2)</td> <td>(53)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>(40)</td> <td>(8)</td> </tr> <tr> <td>H</td> <td>OPh</td> <td>(—)</td> <td>(62)</td> </tr> <tr> <td>H</td> <td>SPh</td> <td>(36)</td> <td>(13)</td> </tr> <tr> <td>H</td> <td>OC₆H₁₁</td> <td>(—)</td> <td>(67)</td> </tr> <tr> <td>Me</td> <td>Ph</td> <td>(12)</td> <td>(15)</td> </tr> </tbody> </table>	R ¹	R ²	I (%)	II (%)	H	CH=CH ₂	(48)	(20)	H	OAc	(6)	(63)	H	Et	(27)	(3)	H	OEt	(6)	(62)	H	CH=CHMe (Z)	(35)	(20)	H	CH=CHMe (E)	(27)	(18)	Me	CH=CH ₂	(60)	(—)	Me	OAc	(6)	(36)	H	OC ₄ H _{9-i}	(2)	(53)	H	Ph	(40)	(8)	H	OPh	(—)	(62)	H	SPh	(36)	(13)	H	OC ₆ H ₁₁	(—)	(67)	Me	Ph	(12)	(15)	353, 354
R ¹	R ²	I (%)	II (%)																																																													
H	CH=CH ₂	(48)	(20)																																																													
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H	OC ₆ H ₁₁	(—)	(67)																																																													
Me	Ph	(12)	(15)																																																													

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

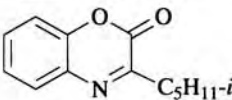
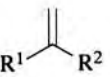
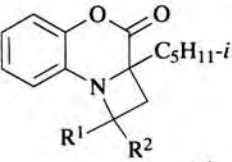
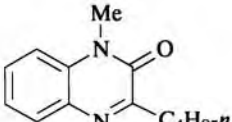
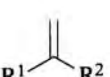
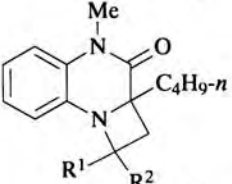
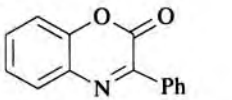
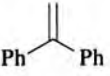
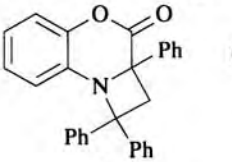
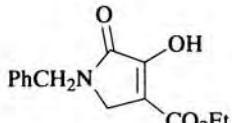

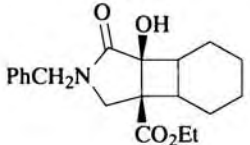
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.												
		Pyrex, C ₆ H ₆ , 25°	 <table border="1" data-bbox="1159 1428 1354 1536"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Me</td> <td>CN</td> <td>(49)</td> </tr> <tr> <td>Me</td> <td>CO₂Me</td> <td>(79)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(56)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Me	CN	(49)	Me	CO ₂ Me	(79)	Ph	Ph	(56)	344
R ¹	R ²	Yield (%)														
Me	CN	(49)														
Me	CO ₂ Me	(79)														
Ph	Ph	(56)														
		>300 nm, C ₆ H ₆	 <table border="1" data-bbox="1159 1719 1354 1809"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>4-C₅H₄N</td> <td>(98)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(26)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	4-C ₅ H ₄ N	(98)	Ph	Ph	(26)	336, 345			
R ¹	R ²	Yield (%)														
H	4-C ₅ H ₄ N	(98)														
Ph	Ph	(26)														
		Pyrex, C ₆ H ₆ , 25°	 (39)	344												
		Pyrex	 (31)	347												

TABLE XI. AZAENONES AND ALKENES OR ACETYLENES (Continued)

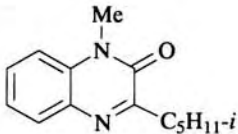
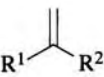
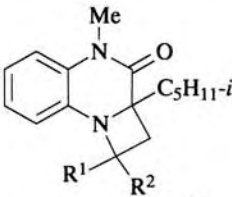
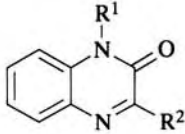
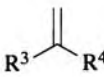
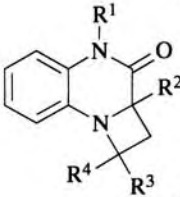
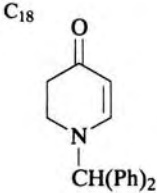
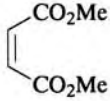
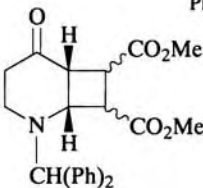
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																			
		>300 nm, C ₆ H ₆	 <table border="1" data-bbox="1159 959 1367 1097"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>4-C₅H₄N</td> <td>(70)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(27)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(80)</td> </tr> <tr> <td>Ph</td> <td>Ph</td> <td>(78)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	4-C ₅ H ₄ N	(70)	Ph	Ph	(27)	Ph	Ph	(80)	Ph	Ph	(78)	336, 345																				
R ¹	R ²	Yield (%)																																					
H	4-C ₅ H ₄ N	(70)																																					
Ph	Ph	(27)																																					
Ph	Ph	(80)																																					
Ph	Ph	(78)																																					
		Pyrex, benzene	 <table border="1" data-bbox="1159 1258 1524 1448"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>Et</td> <td>Ph</td> <td>Ph</td> <td>Ph</td> <td>(70)</td> </tr> <tr> <td>H</td> <td>Ph</td> <td>Me</td> <td>CN</td> <td>(10,65)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>CN</td> <td>(97)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Me</td> <td>CO₂Me</td> <td>(42,39)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>H</td> <td>4-C₅H₄N</td> <td>(85)</td> </tr> <tr> <td>Ph</td> <td>Me</td> <td>Ph</td> <td>Ph</td> <td>(34)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴	Yield (%)	Et	Ph	Ph	Ph	(70)	H	Ph	Me	CN	(10,65)	Ph	Me	Me	CN	(97)	Ph	Me	Me	CO ₂ Me	(42,39)	Ph	Me	H	4-C ₅ H ₄ N	(85)	Ph	Me	Ph	Ph	(34)	336
R ¹	R ²	R ³	R ⁴	Yield (%)																																			
Et	Ph	Ph	Ph	(70)																																			
H	Ph	Me	CN	(10,65)																																			
Ph	Me	Me	CN	(97)																																			
Ph	Me	Me	CO ₂ Me	(42,39)																																			
Ph	Me	H	4-C ₅ H ₄ N	(85)																																			
Ph	Me	Ph	Ph	(34)																																			
		Pyrex	 (60)	334																																			

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES

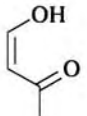

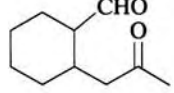

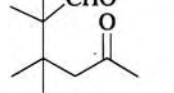
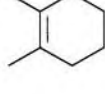

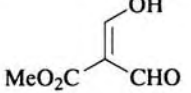

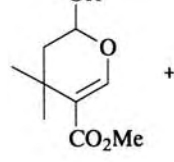
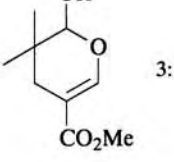

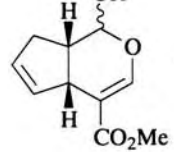
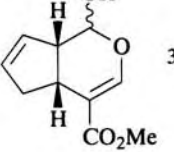
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		Corex or Pyrex, -20°, pentane, 1-2 h	 (—)	355
		Corex or Pyrex, -20°, pentane, 1-2 h	 (80)	355
		Corex or Pyrex, -20°, pentane, 1-2 h	 (—)	356
C_5 		Pyrex, pentane: CH_2Cl_2 (1.5:1), -30°, 5.5 h	 +  3:1 (91)	78
		Corex, CH_3CN	 +  3:7 (60-65)	341

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)


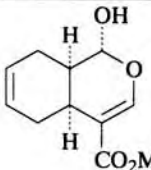
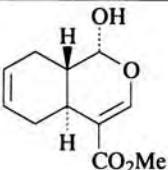

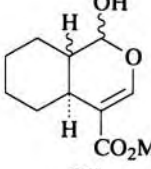

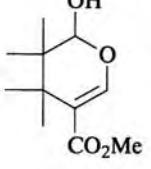
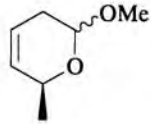
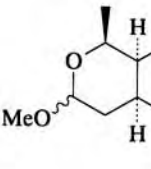
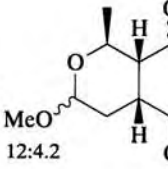
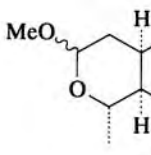
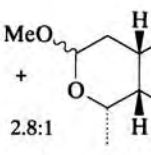
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex	 (62) +  (5)	357
		Pyrex, pentane: CH ₂ Cl ₂ (1.5:1), -30°, 5.5 h	 (85)	162
		Pyrex, pentane: CH ₂ Cl ₂ (1.5:1), -30°, 5.5 h	 (89)	162
		Pyrex, hexane, CH ₂ Cl ₂	 +  + 78 12:4.2  +  (20) 2.8:1	

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)

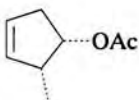
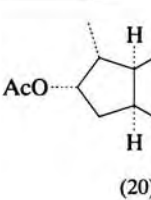
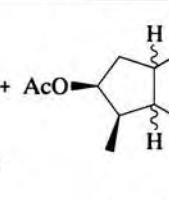
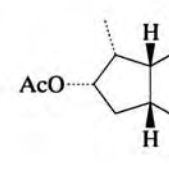
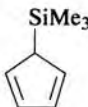
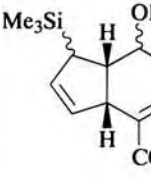
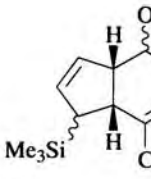
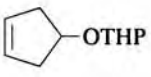
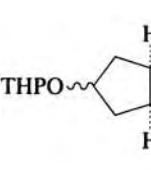
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Corex, 44 h	 (20) +  (13) +  (13)	77
		Corex, CH ₂ Cl ₂ , -35°, 6 h Corex, THF, -35° Corex, CH ₃ CN, -35°	 +  1:2 (60-65) 2:1 (60-65) 0:100 (60-65)	341
		Pyrex, 40 h	 (—)	76

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)

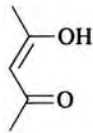
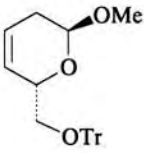
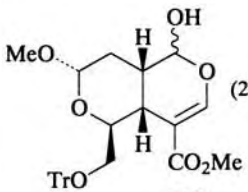
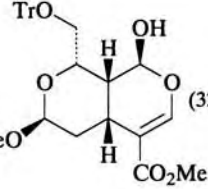
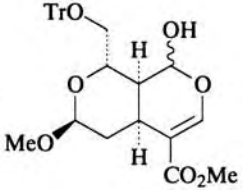
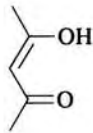

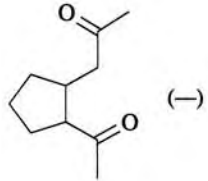
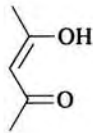

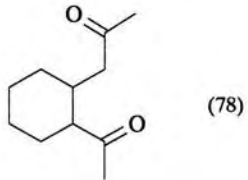
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, cyclohexane, 9 h	 (25) +  (32) 79 +  (5)	
		Pyrex, 95 h	 (—)	358
		Pyrex, 45 h	 (78)	358, 191

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)

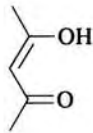

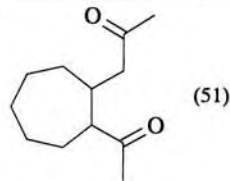
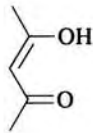

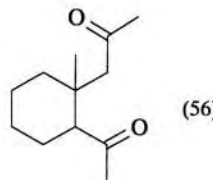
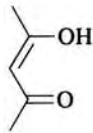

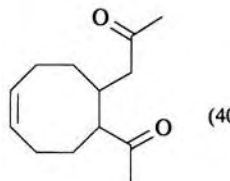
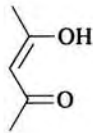
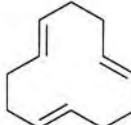
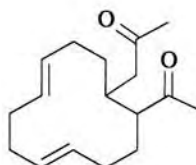
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
		Pyrex, 7 d	 (51)	358, 359
		Pyrex, 56 h	 (56)	358
		4 d	 (40)	359
		—	 (71)	359

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)

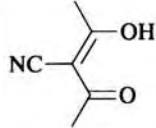

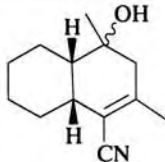
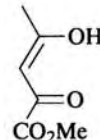

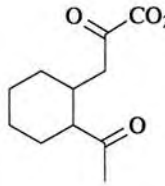

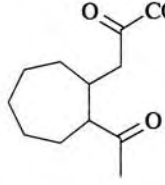
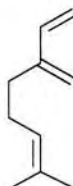
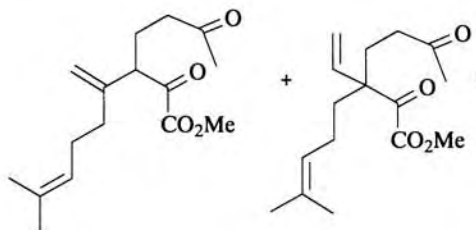
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 		Pyrex, 50-60 h	 (60)	79
		Pyrex, ether	 (95)	360
		Pyrex, ether	 (—)	361
		—	 (—)	362, 363, 364

TABLE XII. ENOLS OF β -DICARBONYLS AND ALKENES (Continued)

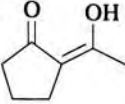

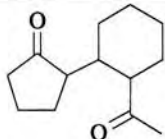
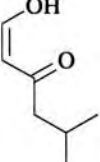

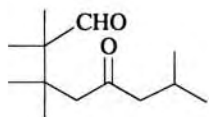
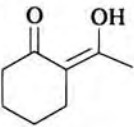

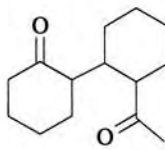
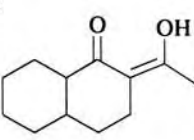

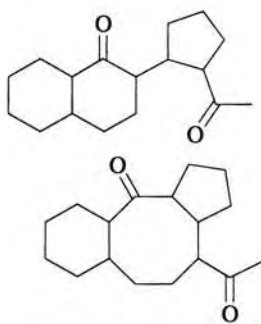
Enone	Alkene	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₇ 		10 d	 (40)	359
		—	 (—)	355
C ₈ 		15 d	 (61)	359
C ₁₂ 		7 d	 (83)	359

TABLE XIII. 2-ALKENYLCYCLOPENTENONES

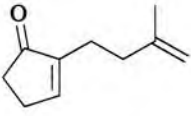
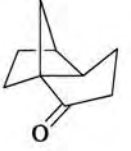
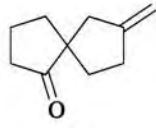
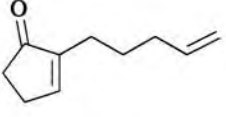
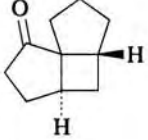
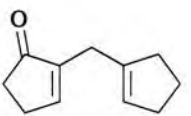
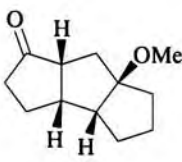
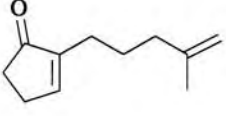
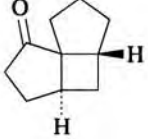
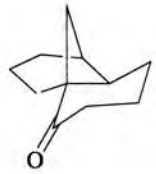
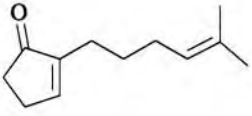
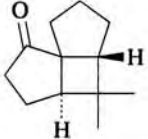
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	Uranium, hexanes	 (50) +  (6)	365
	Uranium, hexanes	 (82)	366
C ₁₁ 	Pyrex, CH ₃ OH	 (60)	367, 368
	Uranium, hexanes	 +  73:27 (63)	366
C ₁₂ 	Uranium, hexanes	 (88)	366

TABLE XIII. 2-ALKENYLCYCLOPENTENONES (Continued)

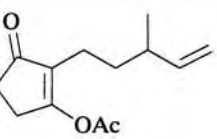
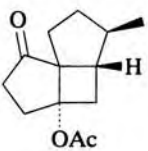
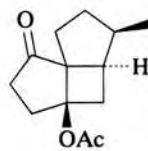
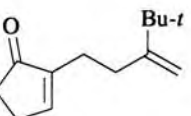
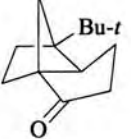
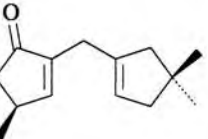
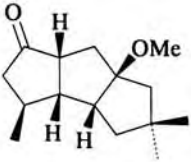
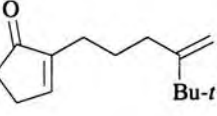
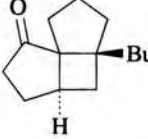
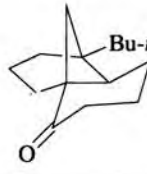
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	Benzene, 3 h	 +  3.3:1 (76)	139
	Uranium, hexanes	 (37)	366
C ₁₄ 	Pyrex, CH ₃ OH	 (60)	369
	Uranium, hexanes	 +  73:27 (63)	366

TABLE XIV. 3-ALKENYLCYCLOPENTENONES

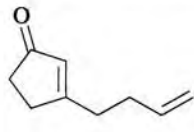
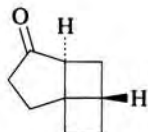
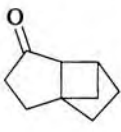
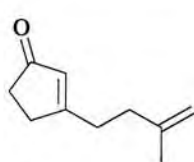
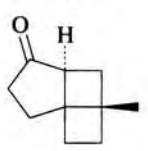
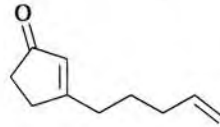
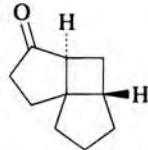
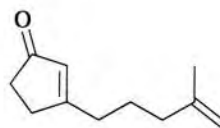
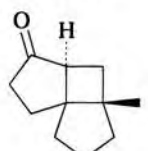
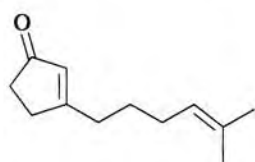
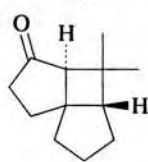
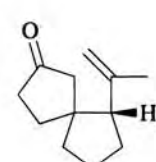
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	Uranium, benzene, 10 d	 (56) +  (7)	103, 104, 105
C ₁₀ 	>340 nm, hexane	 (84)	103, 104, 105
	Uranium, hexanes	 (92)	366
C ₁₁ 	Uranium, hexanes	 (93)	366
C ₁₂ 	Uranium, hexanes	 (50) +  (40)	366

TABLE XIV. 3-ALKENYLCYCLOPENTENONES (Continued)

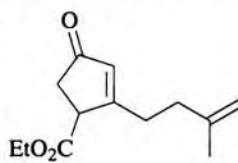
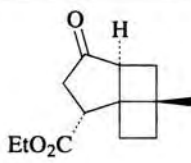
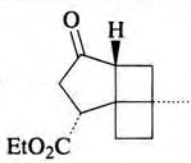
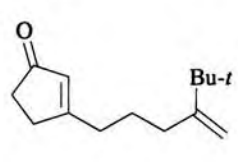
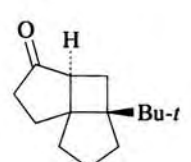
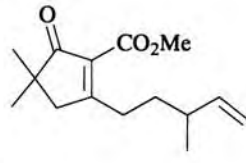
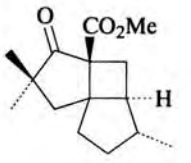
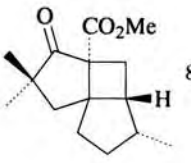
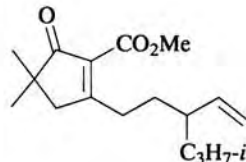
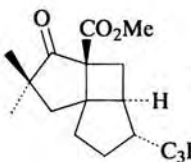
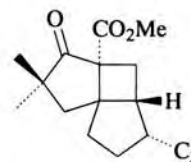
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	>340 nm, hexane	 +  2:1 (82)	103, 104, 105
C ₁₄ 	Uranium, hexanes	 (92)	366
C ₁₅ 	Uranium, hexanes	 +  88:12 (77)	141
C ₁₇ 	Uranium, hexanes	 +  >97:3 (87)	141

TABLE XIV. 3-ALKENYLCYCLOPENTENONES (Continued)

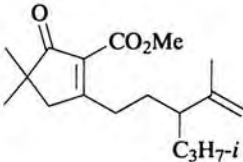
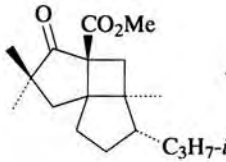
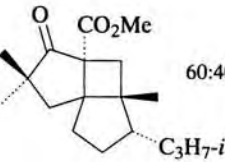
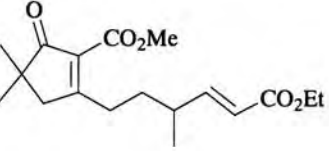
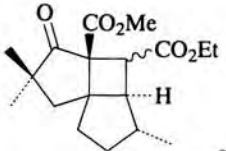
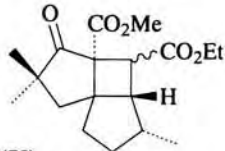
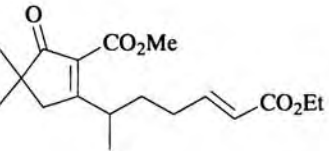
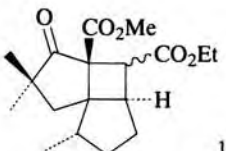
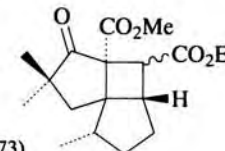
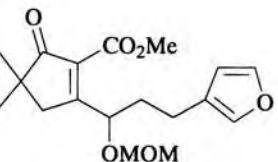
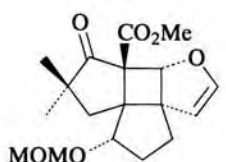
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Uranium, hexanes	 +  60:40 (87)	141
	Uranium, hexanes	 +  88:12 (75)	141
	Uranium, hexanes	 +  13:1 (73)	136, 137
	Uranium, hexanes	 (74)	141

TABLE XIV. 3-ALKENYLCYCLOPENTENONES (Continued)

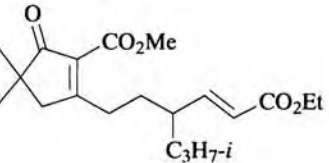
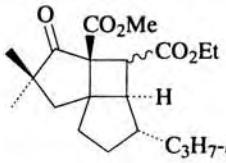
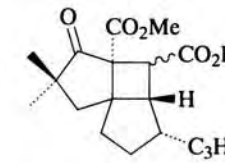
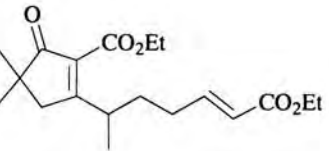
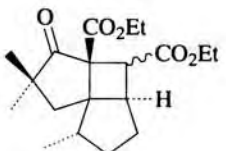
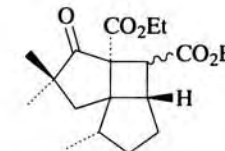
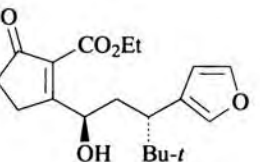
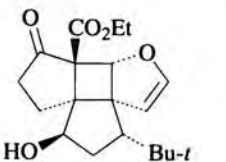
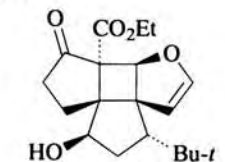
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Uranium, hexanes	 +  >97:3 (82)	141
	Uranium, hexanes	 +  17:1 (70)	141
	Uranium glass	 + 	141
	1:9 benzene:hexanes	1:1.1 (75-80)	
	1:4 CH ₂ Cl ₂ :hexanes	1:2 (75-80)	
	CH ₃ OH	0:100 (75-80)	

TABLE XIV. 3-ALKENYLCYCLOPENTENONES (Continued)

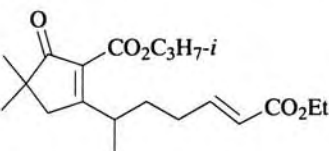
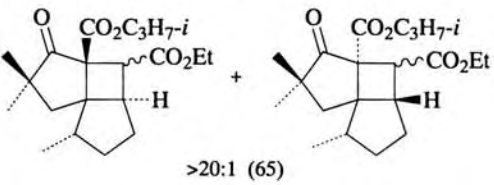
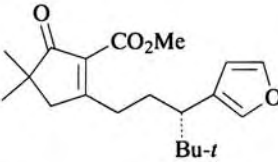
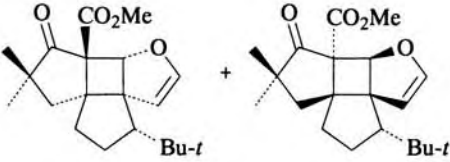
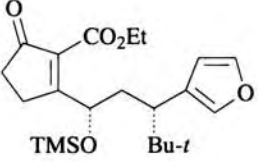
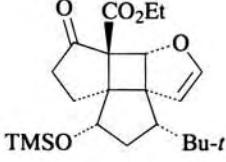
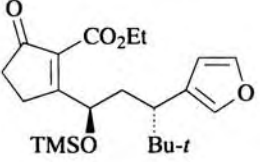
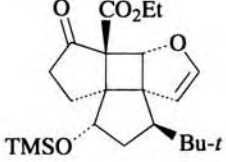
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	Uranium, hexanes	 >20:1 (65)	136, 137
	Uranium glass, hexane	 60:40 (75)	142
C_{22} 	Uranium glass, hexane	 (81)	142
	Uranium glass, hexane	 (83)	142

TABLE XV. 4-ALKENYLCYCLOPENTENONES

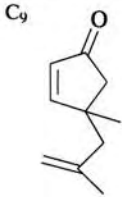
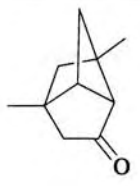
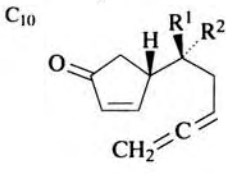
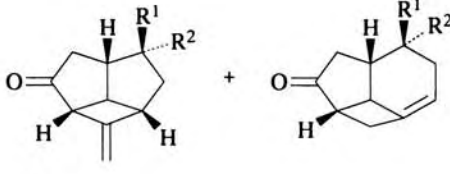
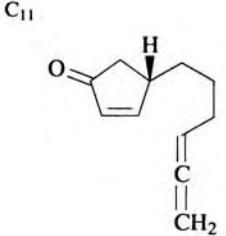
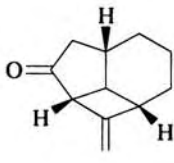
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																								
<p>C₉</p> 	>300 nm, benzene	 <p>(87)</p>	370																								
<p>C₁₀</p> 	Uranium glass, ether	 <table border="1" data-bbox="920 1159 1267 1331"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> <th>Ref.</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>3:1</td> <td>(98)</td> </tr> <tr> <td>H</td> <td>OH</td> <td>4:1</td> <td>(88)</td> </tr> <tr> <td>OH</td> <td>H</td> <td>6:1</td> <td>(77)</td> </tr> <tr> <td>H</td> <td>OTBDMS</td> <td>1.2:1</td> <td>(88)</td> </tr> <tr> <td>OTBDMS</td> <td>H</td> <td>10:1</td> <td>(78)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	Ref.	H	H	3:1	(98)	H	OH	4:1	(88)	OH	H	6:1	(77)	H	OTBDMS	1.2:1	(88)	OTBDMS	H	10:1	(78)	157
R ¹	R ²	Yield (%)	Ref.																								
H	H	3:1	(98)																								
H	OH	4:1	(88)																								
OH	H	6:1	(77)																								
H	OTBDMS	1.2:1	(88)																								
OTBDMS	H	10:1	(78)																								
<p>C₁₁</p> 	Uranium glass, ether	 <p>(—)</p>	157																								

TABLE XV. 4-ALKENYLCYCLOPENTENONES (Continued)

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄		Pyrex, hexane, 15 h	 (86)	371
C ₂₁		THF, -70°, 90 min	 (18)	372

TABLE XVI. 5-ALKENYLCYCLOPENTENONES

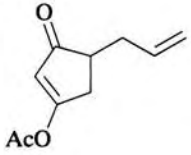
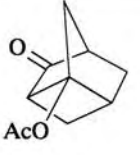
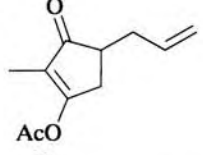
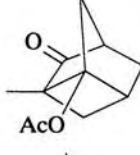
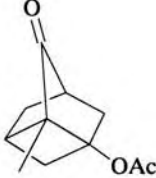
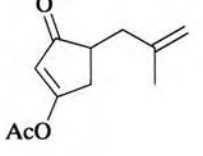
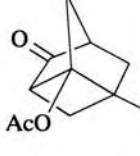
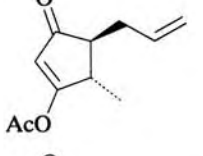
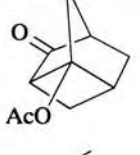
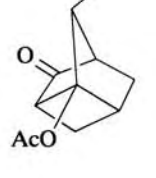
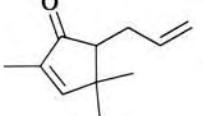
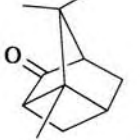
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	Pyrex, hexanes	 (80)	369
C ₁₁ 	Pyrex, hexanes	 +  7:3 (90)	373, 374
	Pyrex, hexanes	 (40)	369
	Pyrex, hexanes	 +  4:1 (82)	373, 374, 369
	Benzene, 3 h	 (90)	375

TABLE XVI. 5-ALKENYLCYCLOPENTENONES (Continued)

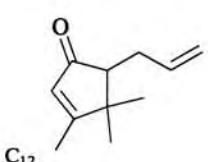
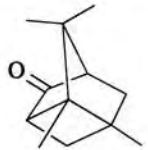
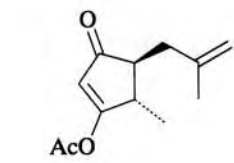
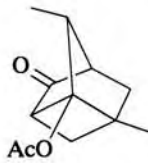
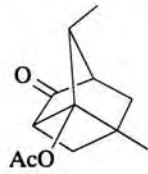
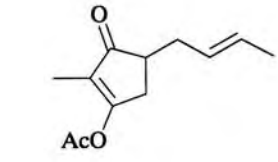
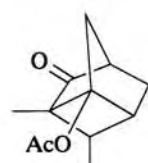
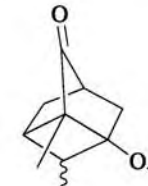
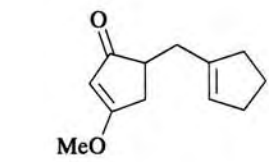
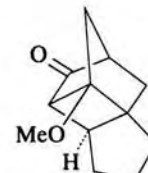

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Benzene, 7 h	 (80)	375
	Pyrex, hexanes	 +  3:2 (72)	369
	Pyrex, hexanes	 +  7:3 (—)	374
	Pyrex, benzene, 15°, 7 h	 +  (—)	374, 376

TABLE XVI. 5-ALKENYLCYCLOPENTENONES (Continued)

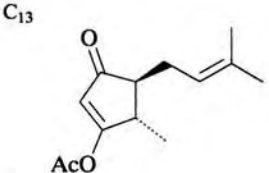

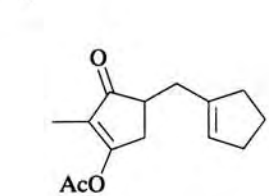
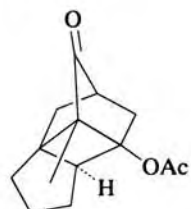
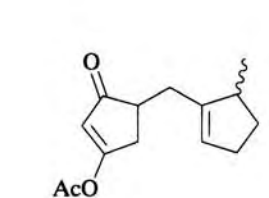
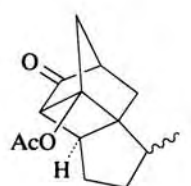
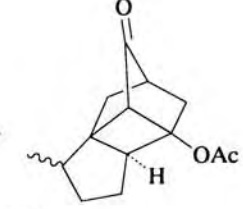
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, hexanes	 (70)	373, 374
	—	 (82)	369
	—	 +  30:70 (—)	374, 377

TABLE XVI. 5-ALKENYLCYCLOPENTENONES (Continued)

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																								
		Benzene, 8 h		378																																								
C ₁₄ C ₁₅			<table border="1"> <thead> <tr> <th>X</th> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>CN</td> <td>H</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>Me</td> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	X	R ¹	R ²	R ³		H	H	H	H	(—)	OMe	H	H	H	(—)	CN	H	H	H	(—)	H	Me	H	H	(—)	H	H	H	Me	(—)	H	Me	Me	H	(—)	H	Me	Me	Me	(—)	
X	R ¹	R ²	R ³																																									
H	H	H	H	(—)																																								
OMe	H	H	H	(—)																																								
CN	H	H	H	(—)																																								
H	Me	H	H	(—)																																								
H	H	H	Me	(—)																																								
H	Me	Me	H	(—)																																								
H	Me	Me	Me	(—)																																								
C ₁₆ C ₁₇																																												
C ₂₂		Pyrex, benzene	 (22)	379																																								
		Pyrex, benzene	 (15)	379																																								

TABLE XVII. DIQUINANE ENONES

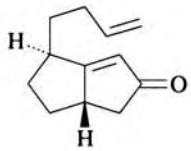
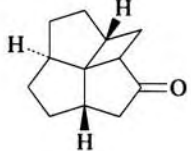
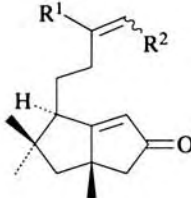
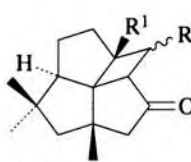
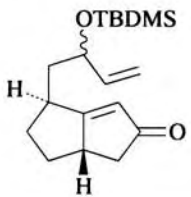
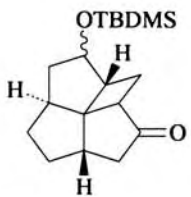
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																					
C_{12} 	>330 nm, 25°, 68 h	 (95)	380																					
	Uranium, hexane, 25° Uranium, hexane, 25° Uranium, chlorobenzene, 110° Uranium, chlorobenzene, 110° Uranium, chlorobenzene, 110° Uranium, chlorobenzene, 110°	 <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>(94)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>(85)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>(65)</td> </tr> <tr> <td>Me</td> <td>CO₂Et</td> <td>(87)</td> </tr> <tr> <td>Me</td> <td>CH₂OCH₂Ph</td> <td>(75)</td> </tr> <tr> <td>Me</td> <td>CH₂OTBDMS</td> <td>(80)</td> </tr> </tbody> </table>	R ¹	R ²		H	H	(94)	H	OMe	(85)	Me	H	(65)	Me	CO ₂ Et	(87)	Me	CH ₂ OCH ₂ Ph	(75)	Me	CH ₂ OTBDMS	(80)	149,150 150 149 151 381 318
R ¹	R ²																							
H	H	(94)																						
H	OMe	(85)																						
Me	H	(65)																						
Me	CO ₂ Et	(87)																						
Me	CH ₂ OCH ₂ Ph	(75)																						
Me	CH ₂ OTBDMS	(80)																						
	>330 nm, 25°, 68 h	 (95)	140																					

TABLE XVIII. OXYGEN TETHERED 2-ALKENYLCYCLOPENTENONES

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.												
	>340 nm, hexane or benzene		382												
C ₈ C ₉ C ₁₀		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>1.6:1 (20)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>1.1:1 (25)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>50:1 (65)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	H	H	1.6:1 (20)	H	Me	1.1:1 (25)	Me	Me	50:1 (65)	
R ¹	R ²	Yield (%)													
H	H	1.6:1 (20)													
H	Me	1.1:1 (25)													
Me	Me	50:1 (65)													
	Acetone, 350 nm, 7 h		383												
C ₁₁ C ₁₂ C ₁₃		<table border="1"> <thead> <tr> <th>n</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>2</td> <td>(97)</td> </tr> <tr> <td>3</td> <td>(84)</td> </tr> <tr> <td>4</td> <td>(73)</td> </tr> <tr> <td>5</td> <td>(30-40)</td> </tr> </tbody> </table>	n	Yield (%)	2	(97)	3	(84)	4	(73)	5	(30-40)			
n	Yield (%)														
2	(97)														
3	(84)														
4	(73)														
5	(30-40)														

TABLE XIX. OXYGEN TETHERED 3- ALKENYLCYCLOPENTENONES

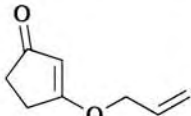
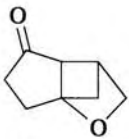
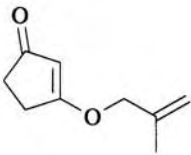
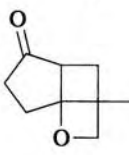
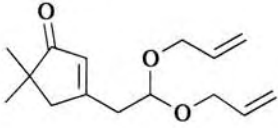
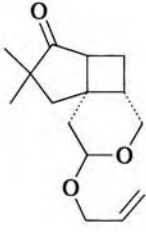
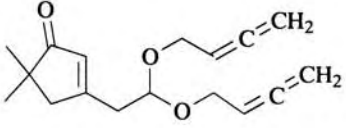
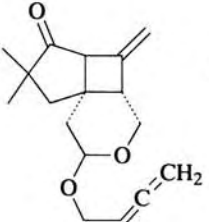
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈		>340 nm, hexane or benzene	 (95)	384
C ₉		>340 nm, hexane or benzene	 (20)	384
C ₁₅		Pyrex, CH ₂ Cl ₂	 (81)	117
C ₁₇		Pyrex, CH ₂ Cl ₂	 (70)	117

TABLE XIX. OXYGEN TETHERED 3-ALKENYLCYCLOPENTENONES (Continued)

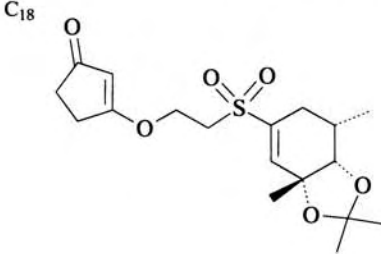
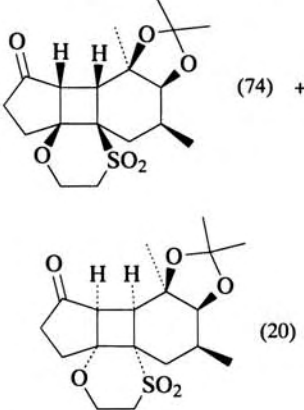
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Vycor, CH ₃ CN, 25°, 40 min		114

TABLE XX. OXYGEN TETHERED 4-ALKENYLCYCLOPENTENONES

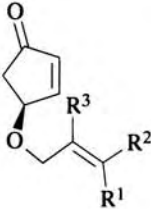
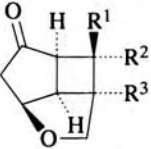
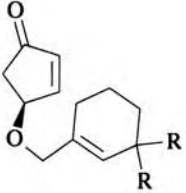
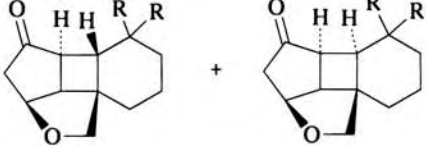
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																				
 <p>C₈ C₉ C₁₀ C₁₁</p>	310 nm, pentane, -25°	 <table border="1" data-bbox="1003 1037 1249 1175"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>(95)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>(80)</td> </tr> <tr> <td>Me</td> <td>Me</td> <td>H</td> <td>(80)</td> </tr> <tr> <td>H</td> <td>—(CH₂)—</td> <td></td> <td>(60)</td> </tr> </tbody> </table>	R ¹	R ²	R ³		H	H	H	(95)	H	H	Me	(80)	Me	Me	H	(80)	H	—(CH ₂)—		(60)	385
R ¹	R ²	R ³																					
H	H	H	(95)																				
H	H	Me	(80)																				
Me	Me	H	(80)																				
H	—(CH ₂)—		(60)																				
 <p>C₁₂ C₁₃</p>	310 nm, pentane, -25°, 5 h 310 nm, pentane, 25°, 9 h	 <table border="1" data-bbox="1050 1441 1232 1496"> <tbody> <tr> <td>R = H</td> <td>35:65</td> <td>(85)</td> </tr> <tr> <td>R = Me</td> <td>40:60</td> <td>(92)</td> </tr> </tbody> </table>	R = H	35:65	(85)	R = Me	40:60	(92)	385														
R = H	35:65	(85)																					
R = Me	40:60	(92)																					

TABLE XXI. 2-ALKENYLCYCLOHEXENONES

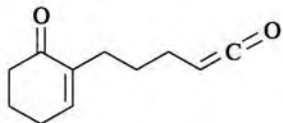
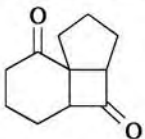
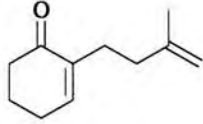

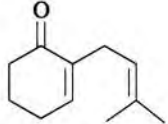
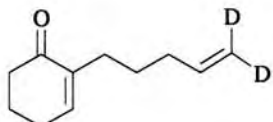
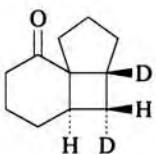
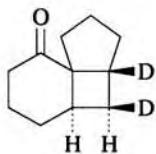
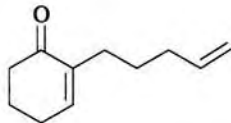
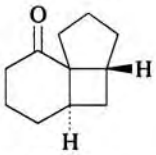
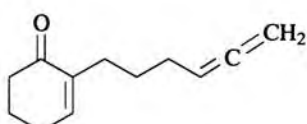
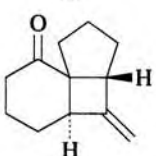
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	>300 nm	 (39)	386
	—	 (71) +  (5)	365
	Uranium, benzene, 2 h	 +  1:2 (95)	387, 388
	Hexane	 (83)	389
C ₁₂ 	Pyrex, cyclohexane, 1 h	 (—)	120

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

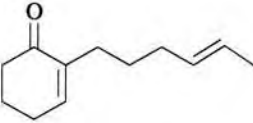
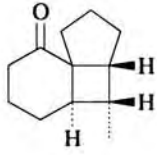
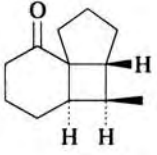
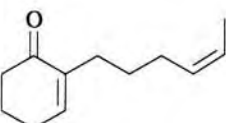
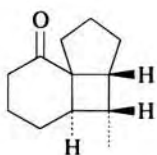
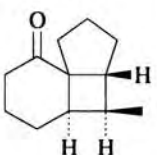
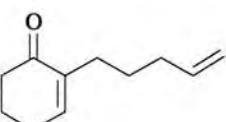
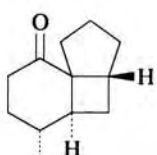
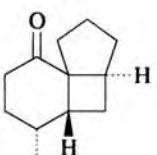
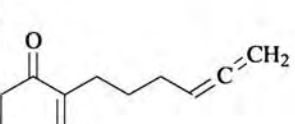
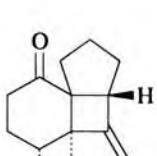
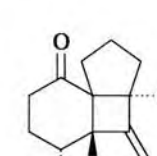
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Uranium, benzene, 2 h	 +  1:35 (92)	387, 388
	Uranium, benzene, 2 h	 +  1:5.8 (92)	387, 388
	Uranium, cyclohexane	 +  1.4:1 (—)	145
C ₁₃ 	Pyrex, cyclohexane, 1 h	 +  3:1 (—)	145

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

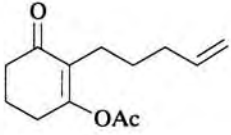
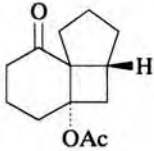
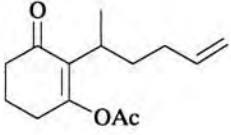
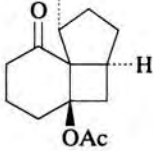
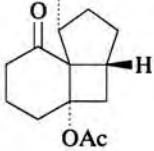
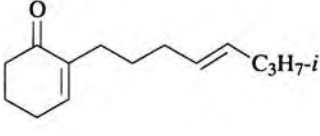
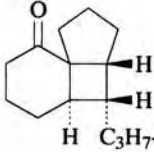
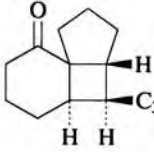
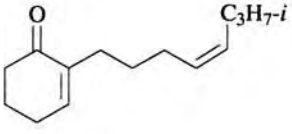
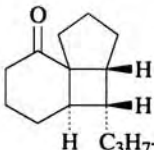
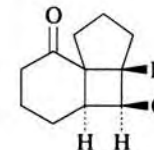
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Uranium, benzene, 2 h	 (95)	390, 391 392 128
	Uranium, benzene, 2 h	 +  92:8 (98)	135
	Uranium, benzene, 2 h	 +  1:3.5 (—)	387, 388
	Uranium, benzene, 2 h	 +  1:1.5 (—)	387, 388

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

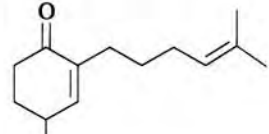
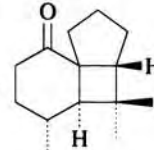
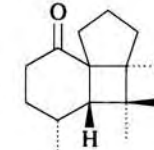
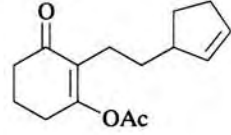
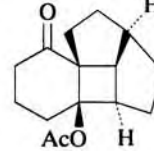
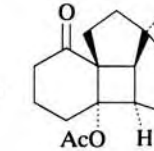
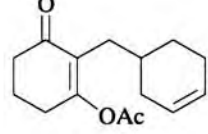
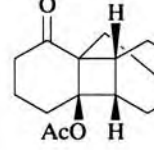
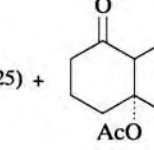
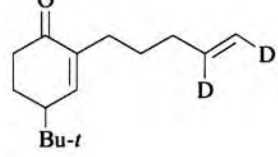
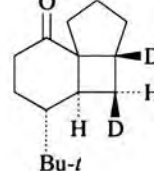
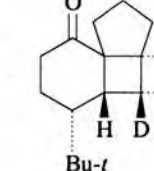
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Uranium, cyclohexane	 +  2.3:1 (—)	145
	Pyrex, cyclohexane, 15-30°	 +  5.8:1 (82)	128
	Pyrex, cyclohexane	 (25) +  (55)	128
	Uranium, cyclohexane	 +  2:1 (—)	145

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

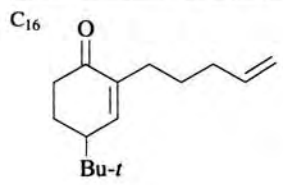
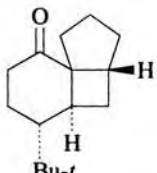
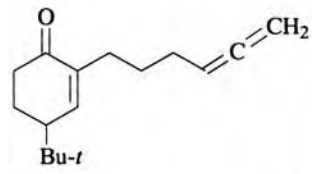
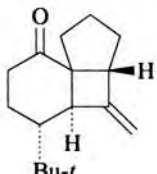
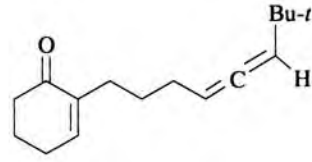
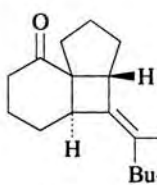
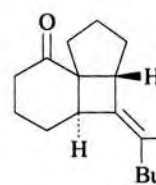
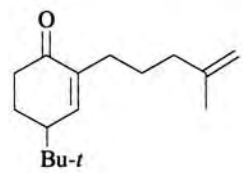
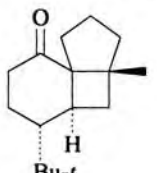
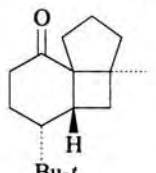
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₆ Bu-t	Uranium, cyclohexane	 (-)	145
 Bu-t	Pyrex, cyclohexane	 (-)	145
 Bu-t	>330 nm	 +  10:1 (90)	387
 Bu-t	Uranium, cyclohexane	 +  2.7:1 (-)	145

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

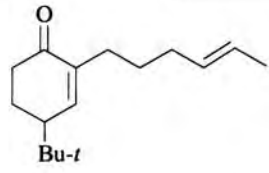
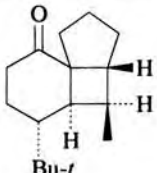
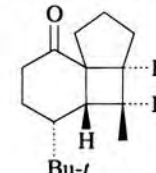
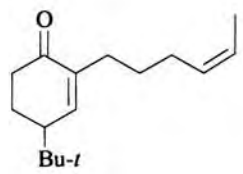
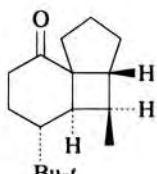
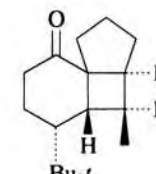
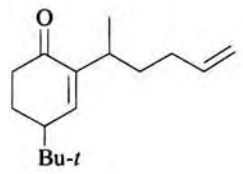
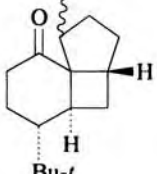
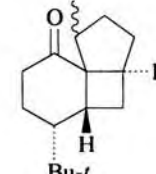
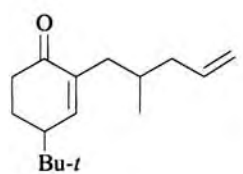
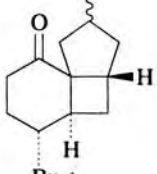
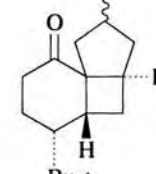
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 Bu-t	Uranium, cyclohexane	 +  4:1 (-)	387
 Bu-t	Uranium, cyclohexane	 +  1.8:1 (-)	387
 Bu-t	Uranium, cyclohexane	 +  2:1 (-)	387
 Bu-t	Uranium, cyclohexane	 +  2:1 (-)	145

TABLE XXI. 2-ALKENYLCYCLOHEXENONES (Continued)

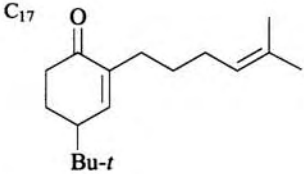
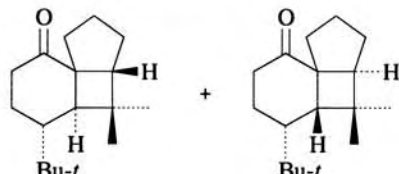
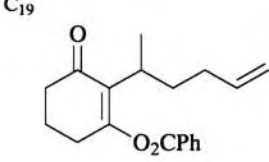
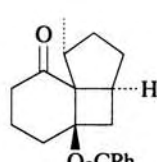
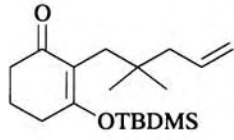
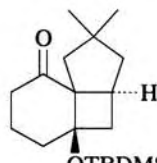
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₇ 	Uranium, cyclohexane	 3:1 (—)	145
C ₁₉ 	Pyrex, hexane	 (98)	392
	Pyrex, heptane	 (81)	109

TABLE XXII. 3-ALKENYLCYCLOHEXENONES

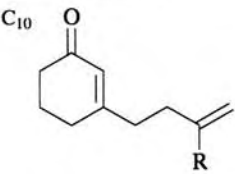
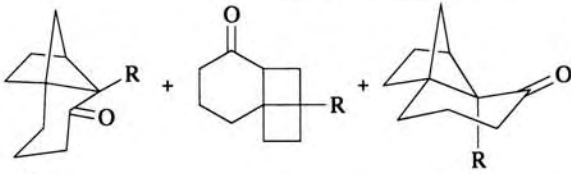
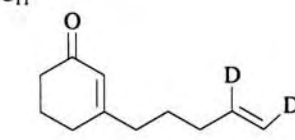
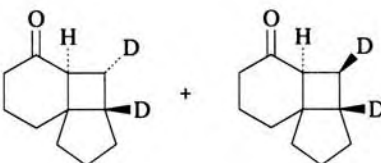
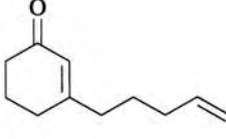
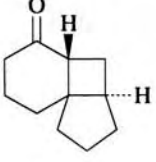
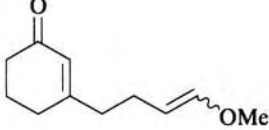
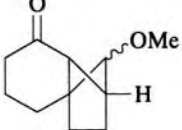
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs																				
	<p>—</p> <p>—</p> <p>366 nm, cyclohexane</p>	 <table border="1"> <thead> <tr> <th>R</th> <th>(49)</th> <th>(22)</th> <th>(20)</th> <th>105</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>(49)</td> <td>(22)</td> <td>(20)</td> <td>105</td> </tr> <tr> <td>Me</td> <td>(11)</td> <td>(76)</td> <td>(0)</td> <td>105</td> </tr> <tr> <td>OMe</td> <td>(0)</td> <td>(75)</td> <td>(0)</td> <td>393</td> </tr> </tbody> </table>	R	(49)	(22)	(20)	105	H	(49)	(22)	(20)	105	Me	(11)	(76)	(0)	105	OMe	(0)	(75)	(0)	393	
R	(49)	(22)	(20)	105																			
H	(49)	(22)	(20)	105																			
Me	(11)	(76)	(0)	105																			
OMe	(0)	(75)	(0)	393																			
	Uranium, benzene, 2 h	 1:1 (95)	388																				
	Hexane	 (92)	389																				
	366 nm, cyclohexane	 (85)	393																				

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

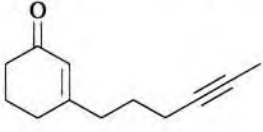
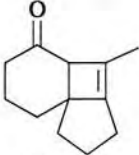
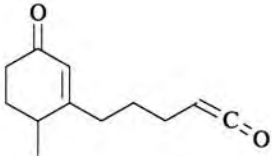
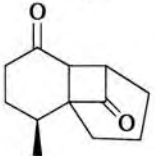
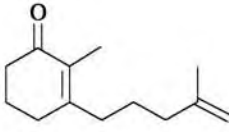
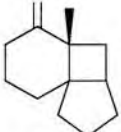
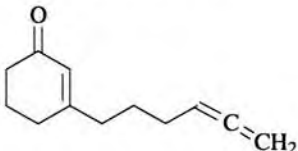
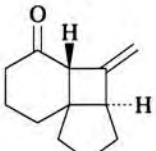
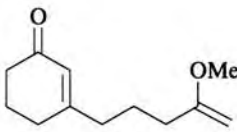
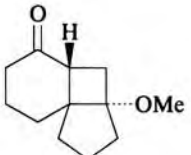
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂ 	Uranium glass, hexane, 7 h	 (64)	394 221
	>300 nm	 (34)	386
	310 nm, CH ₃ OH or benzene	 (75)	395
	Pyrex, cyclohexane, 45 min	 (95)	120
	366 nm, cycl ohexane	 (76)	393

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

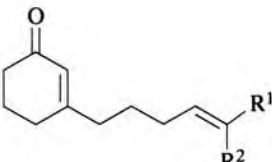
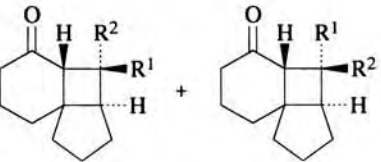
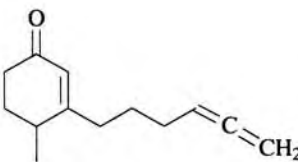
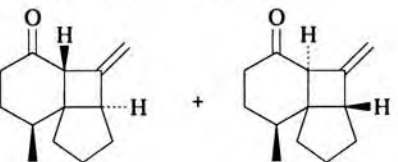
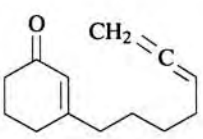
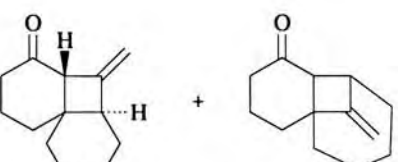
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.											
	Pyrex, benzene, 1.5 h		396											
	Pyrex	<table border="1" data-bbox="980 1503 1102 1687"> <thead> <tr> <th>R¹</th> <th>R²</th> </tr> </thead> <tbody> <tr> <td>CH₂Cl</td> <td>H</td> </tr> <tr> <td>H</td> <td>Me</td> </tr> <tr> <td>Me</td> <td>H</td> </tr> <tr> <td>OMe</td> <td>H</td> </tr> </tbody> </table>	R ¹	R ²	CH ₂ Cl	H	H	Me	Me	H	OMe	H	1:1 (high yield)	134
R ¹	R ²													
CH ₂ Cl	H													
H	Me													
Me	H													
OMe	H													
	Pyrex	Me H	1:1 (high yield)	134										
	366 nm, cyclohexane	OMe H	(80)	393										
C ₁₃ 	Pyrex, cyclohexane, 45 min	 1.6:1 (95)	120											
	Pyrex, cyclohexane, 45 min	 85:15 (100)	120											

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

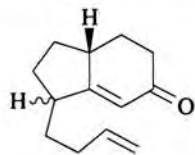
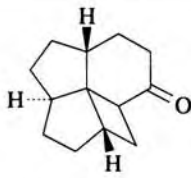
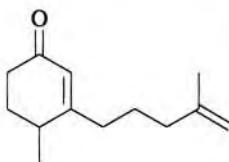
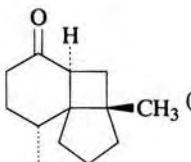
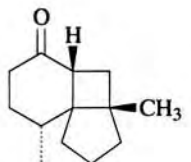
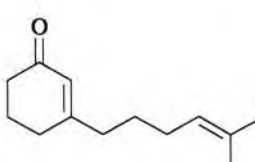
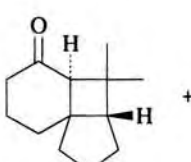
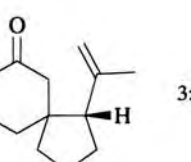
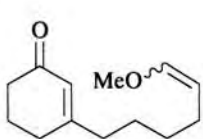
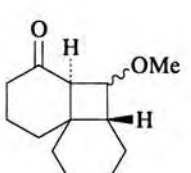
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Hexane, 4.5 h	 (—)	152
	350 nm, hexane	 (64) +  (33)	146
	>300 nm, pentane 350 nm, cyclohexane, 25°	 +  3:1 (77)	397
	366 nm, cyclohexane	 (93)	393

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

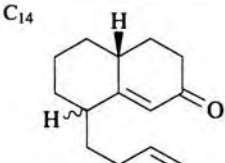
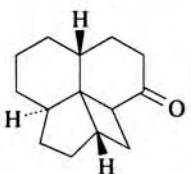
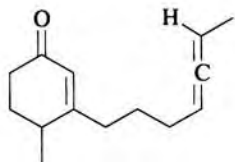
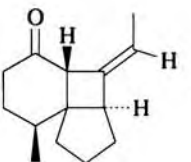
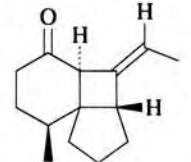
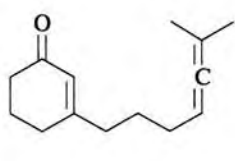
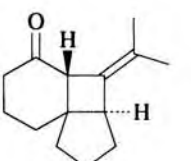
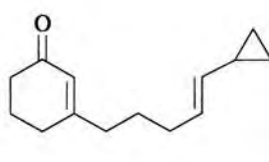
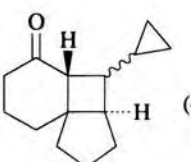
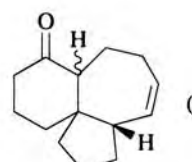
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
^{C14} 	Hexane, 4.5 h	 (—)	152
	Pyrex, cyclohexane, 1 h	 +  1.1:1 (95)	398
	Pyrex, cyclohexane, 1 h	 (62)	398
	Pyrex, cyclohexane, 1 h	 (47) +  (43)	399

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

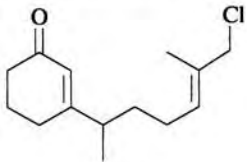
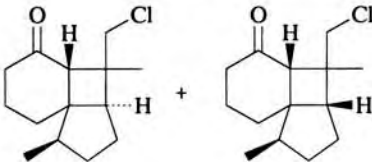
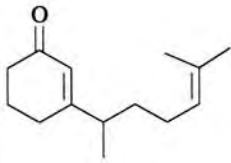
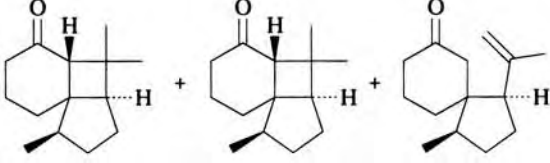
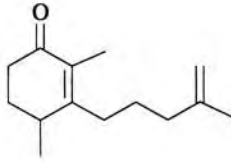
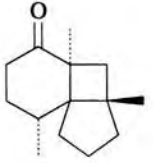
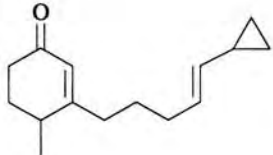
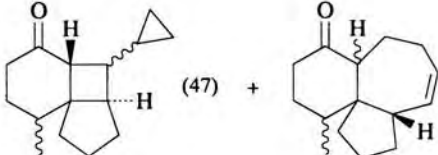
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
	Pyrex	 4:1 (76)	133
	350 nm, cyclohexane, 25° 350 nm, cyclohexane, -78° Pyrex, CH ₂ Cl ₂ , -78°, 1 h	 2:1:2 (52) 5:1:3 (70) 5:1:0 (85)	397 397 400
	350 nm, hexane	 (77)	146
	Pyrex, cyclohexane, 1 h	 (47) + (43)	399

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

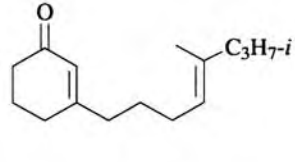
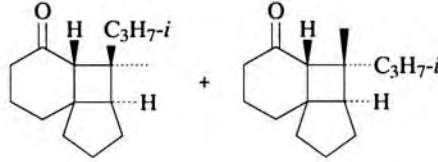
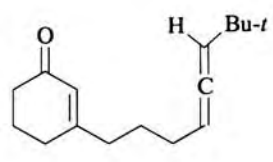
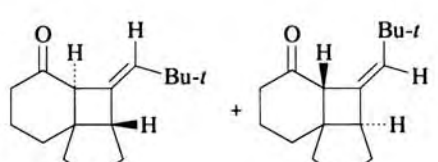
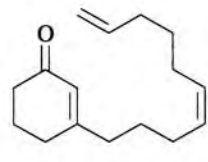
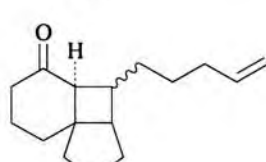
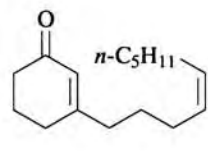
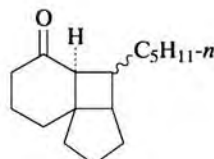
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
	>330 nm	 1:1 (—)	134
	Pyrex, cyclohexane, 2 h	 1.5:1 (87)	398
	Uranium	 (—)	398
	Uranium	 (—)	399

TABLE XXII. 3-ALKENYLCYCLOHEXENONES (Continued)

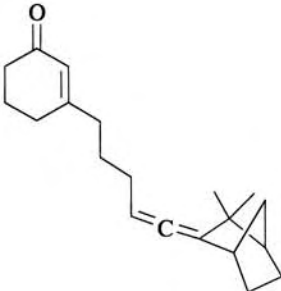
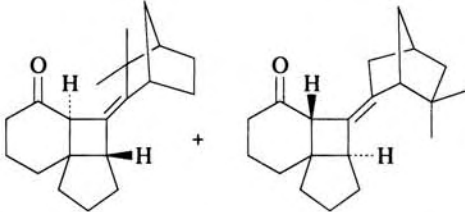
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₀</p> 	Pyrex	 <p>1:1 (56)</p>	398

TABLE XXIII. 4-ALKENYLCYCLOHEXENONES

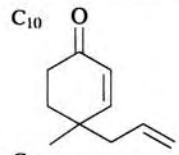
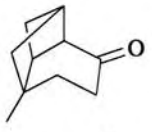
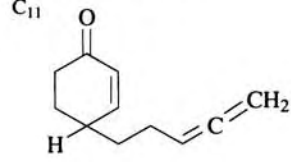
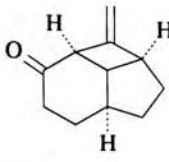
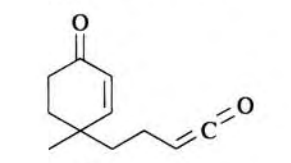
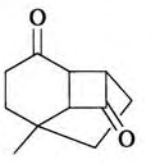
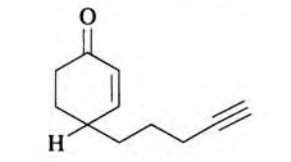
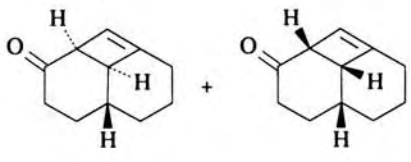
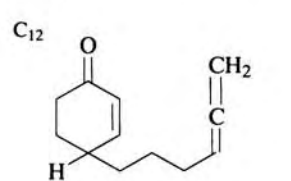
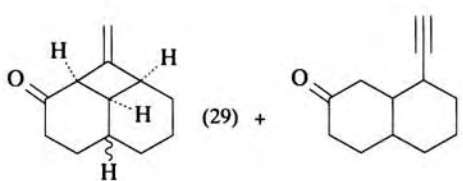
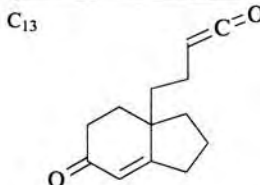
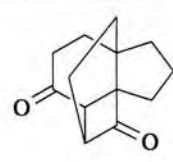
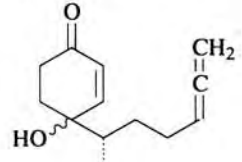
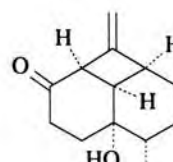
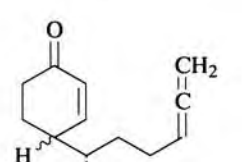
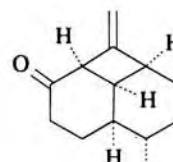
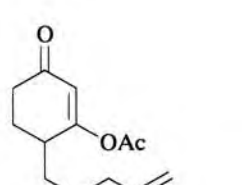
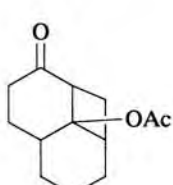
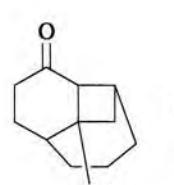
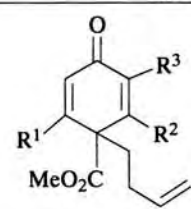
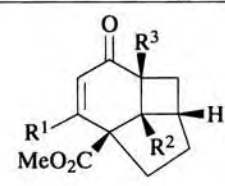
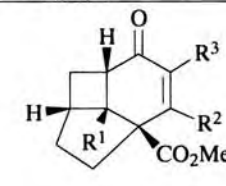
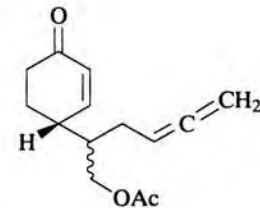
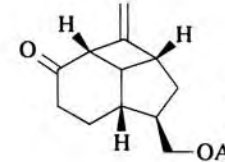
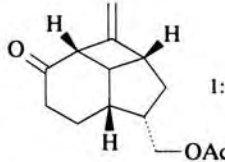
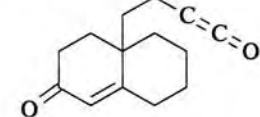
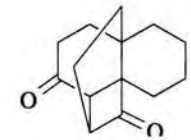
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₁₀	—	 (9)	401
 C ₁₁	Uranium, hexane	 (-)	158
	>300 nm	 (32)	386
	Uranium, hexane	 2:1 (55)	154, 155
 C ₁₂	—	 (29) + (25)	158

TABLE XXIII. 4-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	—	 (31)	386
	Uranium glass, ether, -70°	 (60) + minor isomers (32)	156, 158
	Uranium glass, ether, -70°	 (38) + minor isomers	88
	—	 +  (—)	390

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TABLE XXIII. 4-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																
	366 nm, benzene 366 nm, benzene 366 nm, benzene 366 nm, MeOH 366 nm, HOAc 366 nm 366 nm, MeOH	 +  <table border="1" data-bbox="868 1446 1388 1699"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>OMe</td> <td>H</td> <td>H</td> <td>>95:5 (95)</td> </tr> <tr> <td>OMe</td> <td>OMe</td> <td>H</td> <td>100:0 (100)</td> </tr> <tr> <td>OMe</td> <td>Me</td> <td>H</td> <td>87:13 (—)</td> </tr> <tr> <td></td> <td></td> <td></td> <td>67:33 (—)</td> </tr> <tr> <td></td> <td></td> <td></td> <td>64:36 (—)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>H</td> <td>100:0 (93)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>OMe</td> <td>100:0 (83)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	Yield (%)	OMe	H	H	>95:5 (95)	OMe	OMe	H	100:0 (100)	OMe	Me	H	87:13 (—)				67:33 (—)				64:36 (—)	OMe	H	H	100:0 (93)	OMe	H	OMe	100:0 (83)	402
R ¹	R ²	R ³	Yield (%)																																
OMe	H	H	>95:5 (95)																																
OMe	OMe	H	100:0 (100)																																
OMe	Me	H	87:13 (—)																																
			67:33 (—)																																
			64:36 (—)																																
OMe	H	H	100:0 (93)																																
OMe	H	OMe	100:0 (83)																																
	—	 +  1:1 (—)	158																																
	—	 (40)	386																																

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TABLE XXIII. 4-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	—	(31)	386
	Uranium glass, hexane	+ 1.5:1 (60)	154, 155
	300 nm, 1:1 acetone: <i>t</i> -BuOH, 7.5 h	+ + 1:1:2 (—)	153
	Pyrex, cyclohexane, 1 h	(100)	120

TABLE XXIII. 4-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	—	+ others (—)	158
	366 nm, pentane, -78°	(45)	403
	366 nm, benzene, 25°, 2.5 h	(30) + (46)	402

TABLE XXIII. 4-ALKENYLCYCLOHEXENONES (Continued)

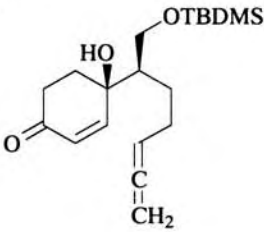
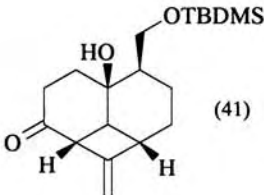
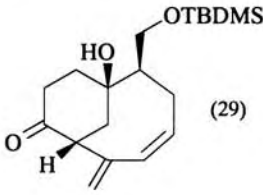
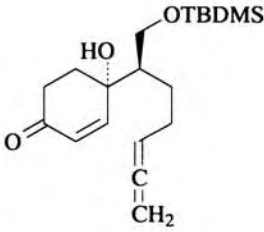
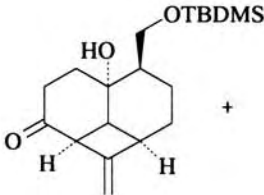
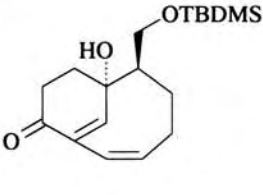
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs
C ₁₉ 	Uranium glass, ether	 (41) +  (29)	88
	Uranium glass, ether, 25° Uranium glass, ether, -78°	 + 	88
		4:1 (—) 9:1 (—)	

TABLE XXIV. 5-ALKENYLCYCLOHEXENONES

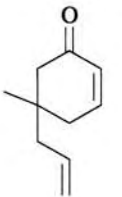
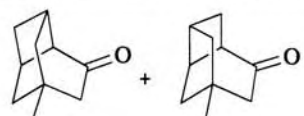
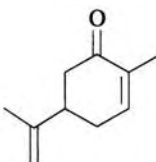
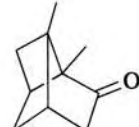
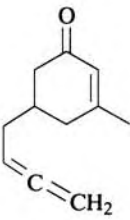
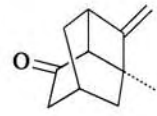
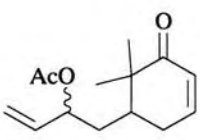
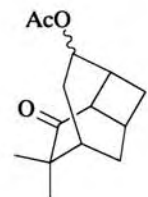
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀		—	 (70)	401
		Sunlight, 1 year	 (9.4) (65)	21, 22 202
C ₁₁		—	 (28)	386
C ₁₄		Pyrex, MeOH, 4 h	 (43)	90

TABLE XXV. 6-ALKENYLCYCLOHEXENONES

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 		+	
C ₁₁ 	Pyrex, cyclohexane Pyrex, MeOH	(35-42) (25)	(-) (49) 404 405
	366 nm, cyclohexane	(-)	197
	Uranium glass, cyclohexane	(74)	406
C ₁₂ 	Pyrex, cyclohexane Pyrex, MeOH	(42) (15)	+ (-) (-) 405

TABLE XXV. 6-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	366 nm, cyclohexane	(-)	197
	366 nm, cyclohexane	(-)	197
	Uranium glass, cyclohexane	(77)	406
	Uranium glass, cyclohexane	(80)	406
	Uranium glass, cyclohexane	(28)	406

TABLE XXV. 6-ALKENYLCYCLOHEXENONES (Continued)

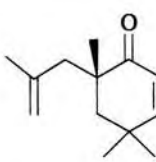
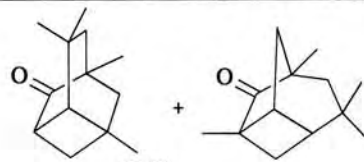
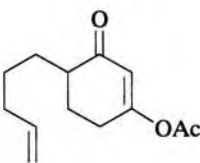
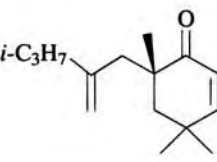
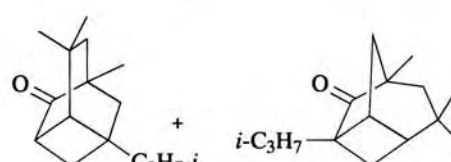
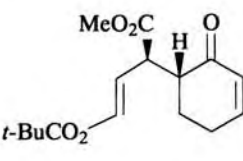
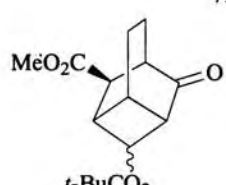
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	366 nm, cyclohexane, CH ₃ CN	 71:29 79:21 (-)	197
	Pyrex, hexanes	(-)	390
C ₁₅ 	366 nm, cyclohexane, CH ₃ CN	 71:29 (-) 79:21 (-)	197
C ₁₆ 	Uranium glass, cyclohexane	 (60)	406

TABLE XXV. 6-ALKENYLCYCLOHEXENONES (Continued)

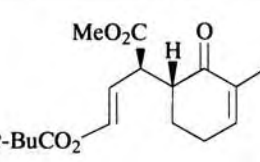
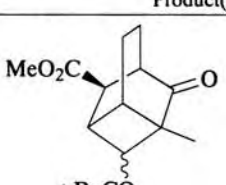
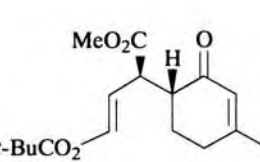
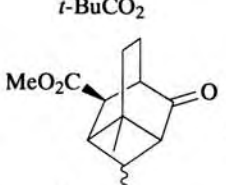
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₇ 	Uranium glass, cyclohexane	 (73)	406
	Uranium glass, cyclohexane	 (61)	406

TABLE XXVI. NITROGEN TETHERED 2-ALKENYLCYCLOHEXENONES

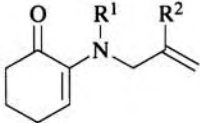
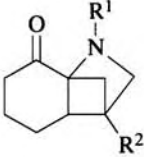
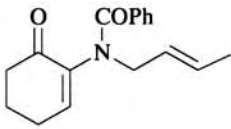
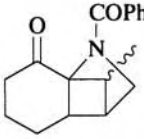
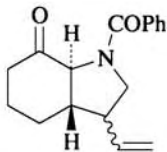
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																		
	Pyrex, acetone	 <table border="1" data-bbox="939 1074 1180 1246"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield (%)</th> </tr> </thead> <tbody> <tr> <td>COMe</td> <td>H</td> <td>(52)</td> </tr> <tr> <td>CO₂Me</td> <td>H</td> <td>(56)</td> </tr> <tr> <td>COC₃H_{7-i}</td> <td>H</td> <td>(26)</td> </tr> <tr> <td>COPh</td> <td>H</td> <td>(61)</td> </tr> <tr> <td>COPh</td> <td>Me</td> <td>(64)</td> </tr> </tbody> </table>	R ¹	R ²	Yield (%)	COMe	H	(52)	CO ₂ Me	H	(56)	COC ₃ H _{7-i}	H	(26)	COPh	H	(61)	COPh	Me	(64)	407
R ¹	R ²	Yield (%)																			
COMe	H	(52)																			
CO ₂ Me	H	(56)																			
COC ₃ H _{7-i}	H	(26)																			
COPh	H	(61)																			
COPh	Me	(64)																			
	Pyrex, acetone	 (25) +  (16)	407																		

TABLE XXVII. NITROGEN TETHERED 3-ALKENYLCYCLOHEXENONES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		Pyrex, acetone	(50-60)	408, 409, 100
C ₁₃		Pyrex, CH ₃ CN, 8 h	(75)	110, 410
C ₁₄		Pyrex, CH ₃ CN, 8 h	(70)	110, 410
		Pyrex, cyclohexane	(69)	100

TABLE XXVII. NITROGEN TETHERED 3-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, acetone	 (57)	110
	Pyrex, CH ₃ CN, 8 h	 (80)	110, 410
	Pyrex, CH ₃ CN, 8 h	 (60)	110, 410
	Pyrex, <i>t</i> -BuOH, 8 h	 (57)	411

TABLE XXVII. NITROGEN TETHERED 3-ALKENYLCYCLOHEXENONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, cyclohexane Pyrex, cyclohexane, 10 h Pyrex, cyclohexane, 2 h	 I II III	110
		R = CHO I (60) + II (9) + III (15) R = Me II (9) R = COMe I (70) + II (8) + III (13)	129 110 129, 412
	Pyrex, <i>t</i> -BuOH, 8 h	 4:1 (78)	413

TABLE XXVIII. OXYGEN TETHERED 2-ALKENYLCYCLOHEXENONES

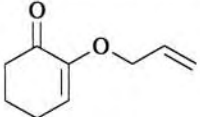
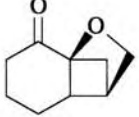
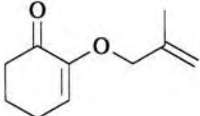
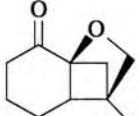
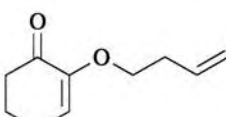
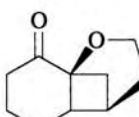
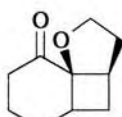
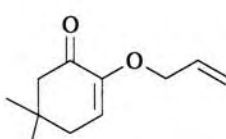
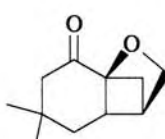
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		Pyrex, acetone, 2 h	 (57)	165
C ₁₀		Pyrex, acetone, 2 h	 (63)	165
		Pyrex, acetone	 (60) +  (7)	165
C ₁₁		Pyrex, acetone, 2 h	 (53)	165

TABLE XXIX. OXYGEN TETHERED 3-ALKENYLCYCLOHEXENONES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉		366 nm, hexane	+ 30:70 (36)	393
		Pyrex, hexane	(54)	384, 408
C ₁₁		366 nm, cyclohexane	(81) + (11)	393
		Pyrex, cyclohexane, 10 h	(70)	408, 409
C ₁₂		Pyrex, hexane	(72)	108, 125

TABLE XXIX. OXYGEN TETHERED 3-ALKENYLCYCLOHEXENONES (Continued)

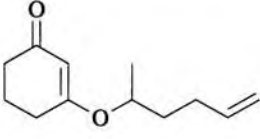
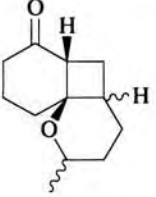
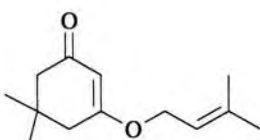
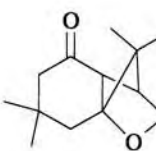
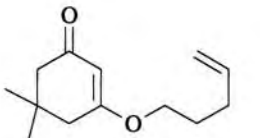
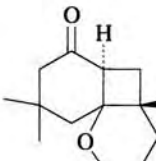
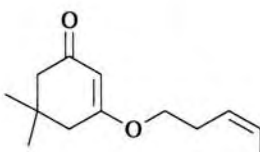
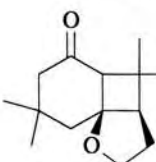
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	366 nm, cyclohexane	 (78)	414
C ₁₃ 	Pyrex, cyclohexane, 15 h	 (69)	100
C ₁₄ 	Pyrex, cyclohexane	 (50-60)	108
	Pyrex, hexane	 (63)	125

TABLE XXIX. OXYGEN TETHERED 3-ALKENYLCYCLOHEXENONES (Continued)

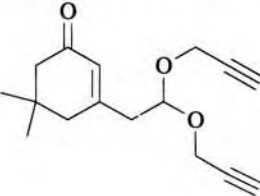
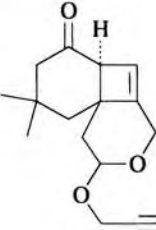
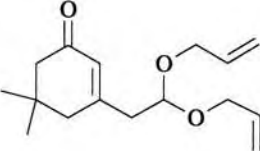
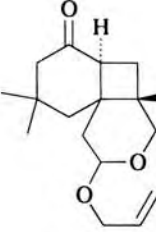
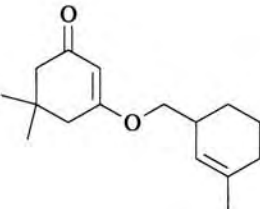
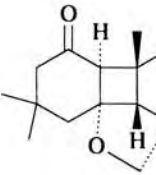
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆ 	Pyrex, CH ₂ Cl ₂	 (58)	117
	Pyrex, CH ₂ Cl ₂	 (75)	117
	Pyrex, hexane	 (47)	125, 415

TABLE XXIX. OXYGEN TETHERED 3-ALKENYLCYCLOHEXENONES (Continued)

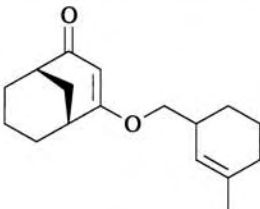
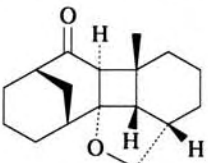
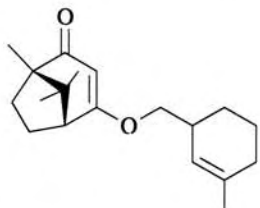
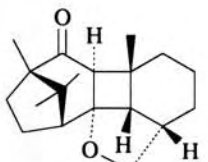
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₇		Pyrex, hexane, 2 h	 (40)	416
C ₁₉		Pyrex, hexane, 15 h	 (60)	72, 73

TABLE XXX. OXYGEN TETHERED 3-ALKENYLCYCLOOCTENONES

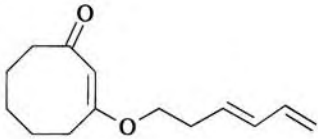
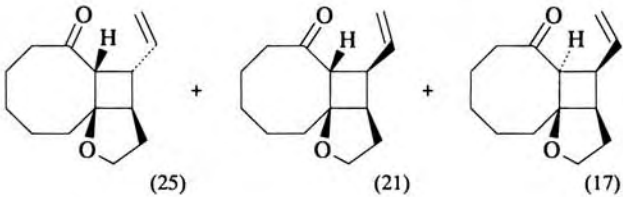
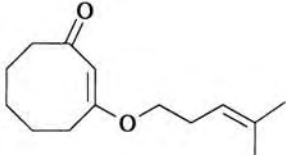
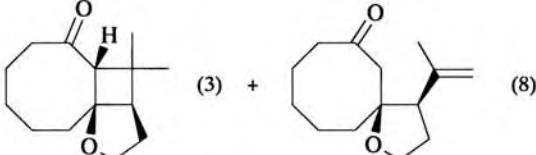
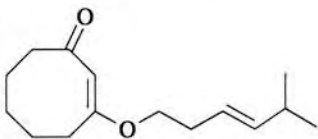
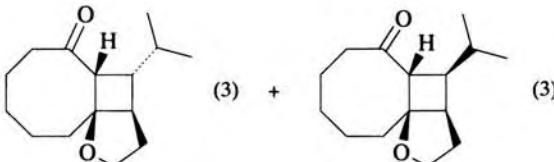
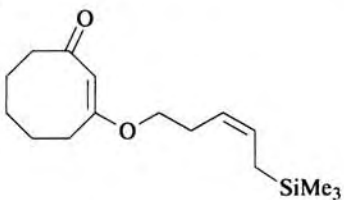
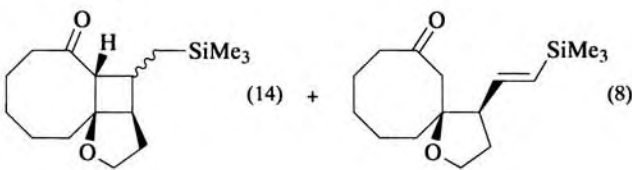
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	350 nm, 6 h	 (25) + (21) + (17)	126
	350 nm, 7 d	 (3) + (8)	126
C ₁₅ 	350 nm, 7 d	 (3) + (3)	126
C ₁₆ 	350 nm	 (14) + (8)	126

TABLE XXX. OXYGEN TETHERED 3-ALKENYLCYCLOOCTENONES (Continued)

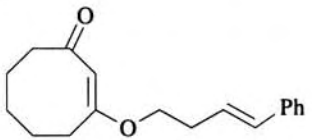
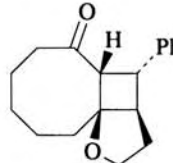
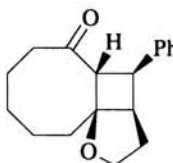
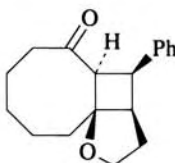
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	350 nm, 6 h	 (21) +  (6) +  (17)	126

TABLE XXXI. BRIDGED BICYCLIC DIENES

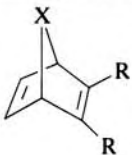
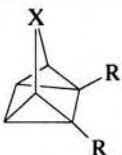
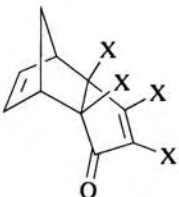
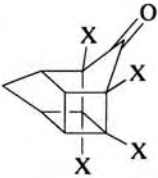
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																														
	—		417 418																														
C ₈		<table border="1"> <thead> <tr> <th>X</th> <th>R</th> <th></th> </tr> </thead> <tbody> <tr> <td>O</td> <td>CF₃</td> <td>(—)</td> </tr> <tr> <td>O</td> <td>CO₂H</td> <td>(—)</td> </tr> <tr> <td>NH</td> <td>CF₃</td> <td>(—)</td> </tr> <tr> <td>NH</td> <td>CO₂H</td> <td>(—)</td> </tr> <tr> <td>CH₂</td> <td>CF₃</td> <td>(—)</td> </tr> <tr> <td>CH₂</td> <td>CO₂H</td> <td>(—)</td> </tr> <tr> <td>O</td> <td>CO₂Me</td> <td>(—)</td> </tr> <tr> <td>NH</td> <td>CO₂Me</td> <td>(—)</td> </tr> <tr> <td>CH₂</td> <td>CO₂Me</td> <td>(—)</td> </tr> </tbody> </table>	X	R		O	CF ₃	(—)	O	CO ₂ H	(—)	NH	CF ₃	(—)	NH	CO ₂ H	(—)	CH ₂	CF ₃	(—)	CH ₂	CO ₂ H	(—)	O	CO ₂ Me	(—)	NH	CO ₂ Me	(—)	CH ₂	CO ₂ Me	(—)	
X	R																																
O	CF ₃	(—)																															
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C ₁₁																																	
C ₁₀																																	
	325-385 nm, benzene benzene	 X = Cl (—) X = H (100)	419 420, 421																														

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

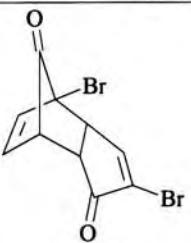
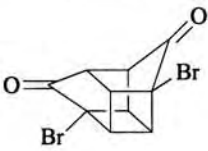
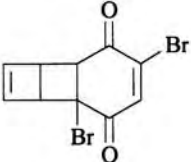
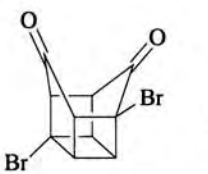
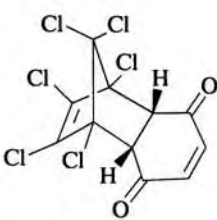
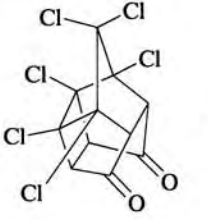
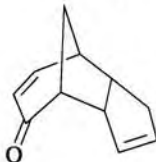
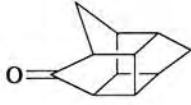
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	MeOH	 (>30)	24
	Benzene	 (80)	422
^{C₁₁} 	EtOAc, 85 h	 (36)	423
	Benzene	 (100)	424

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

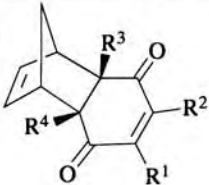
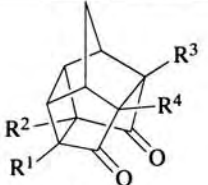
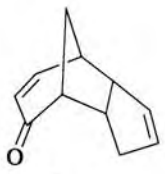
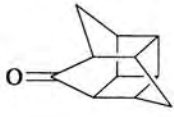
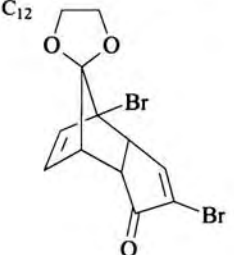
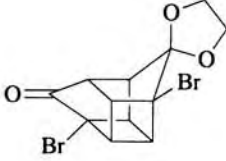
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																																			
	Pyrex, benzene, 20 min		425																																			
		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>Cl</td> <td>Cl</td> <td>Cl</td> <td>(-)</td> </tr> <tr> <td>Br</td> <td>Br</td> <td>Br</td> <td>Br</td> <td>(-)</td> </tr> <tr> <td>Cl</td> <td>Cl</td> <td>H</td> <td>H</td> <td>(-)</td> </tr> <tr> <td>Cl</td> <td>H</td> <td>H</td> <td>Cl</td> <td>(-)</td> </tr> <tr> <td>Br</td> <td>H</td> <td>H</td> <td>Br</td> <td>(-)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(-)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴		Cl	Cl	Cl	Cl	(-)	Br	Br	Br	Br	(-)	Cl	Cl	H	H	(-)	Cl	H	H	Cl	(-)	Br	H	H	Br	(-)	H	H	H	H	(-)	
R ¹	R ²	R ³	R ⁴																																			
Cl	Cl	Cl	Cl	(-)																																		
Br	Br	Br	Br	(-)																																		
Cl	Cl	H	H	(-)																																		
Cl	H	H	Cl	(-)																																		
Br	H	H	Br	(-)																																		
H	H	H	H	(-)																																		
	Benzene	 (94)	424																																			
^{C₁₂} 	Benzene	 (95)	25																																			

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

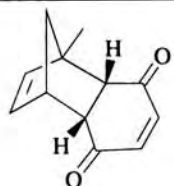

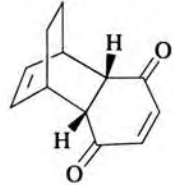

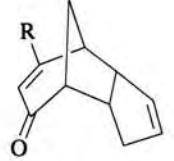
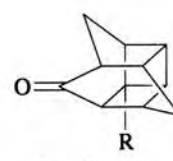
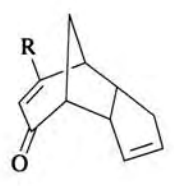
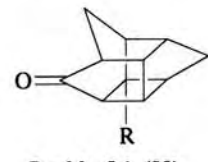
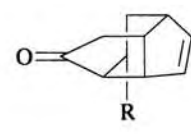
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, EtOAc	 (75)	426
	EtOAc, 10 h	 (75)	426
	Benzene	 (94) R = Me (81) R = OMe (100)	424
	Benzene	 +  R = Me 5:1 (90) R = OMe 100:0 (89)	424

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

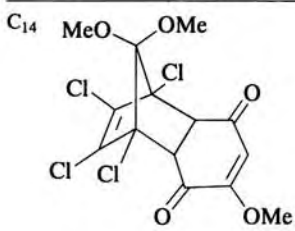
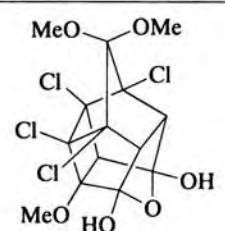
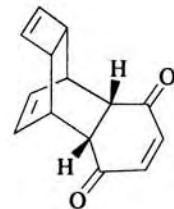
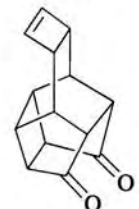
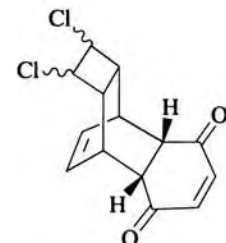
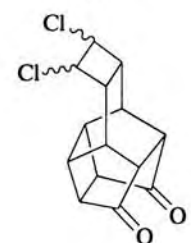
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
^C ₁₄ 	Pyrex, acetone, 2 h	 (73)	23
	EtOAc, 2.5 h	 (90)	423
	EtOAc, 9 h	 (35)	423

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

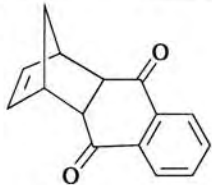
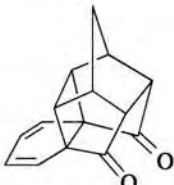
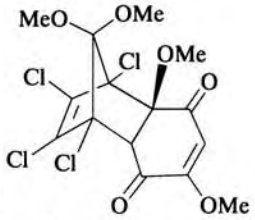
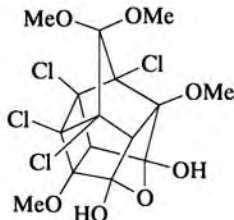
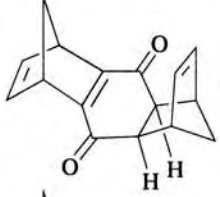
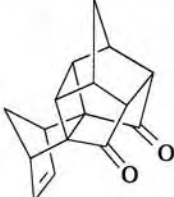
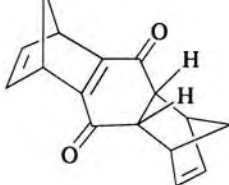

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	—	 (73)	427
	Pyrex, acetone, 2 h	 (81)	23
C ₁₆ 	Pyrex, hexane, 5 h	 (60)	428
	Pyrex, hexane, 5 h	 (60)	428

TABLE XXXI. BRIDGED BICYCLIC DIENES (Continued)

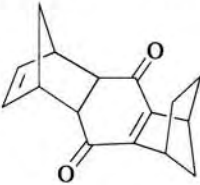
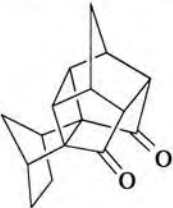
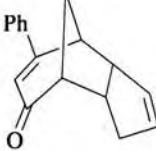
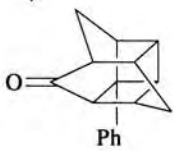
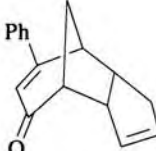
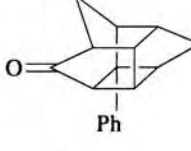
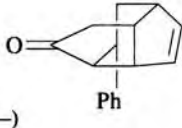
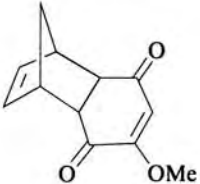
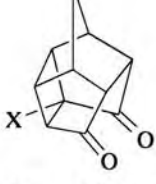
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₇ 	—	 (—)	423
	Benzene	 (40)	424
	Benzene	 +  4:1 (—)	424
C ₁₈ 	Pyrex, acetone, 2 h	 X = <i>p</i> -NCC ₆ H ₄ (98) X = <i>p</i> -MeOC ₆ H ₄ (93)	425

TABLE XXXI. BRIDGED BICYCLIC DIENES (*Continued*)

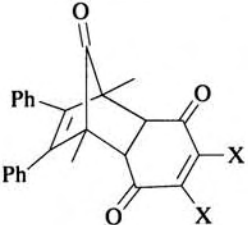
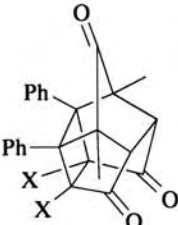
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
<p>C₂₅</p> 	<p>Pyrex, benzene, 20-60 min</p>	 <p>X = Cl (>90) X = H (>90)</p>	425

TABLE XXXII. 3-ALKENYLDIOXOLENONES

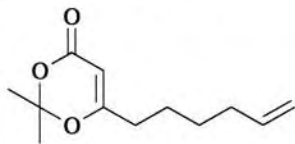
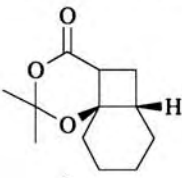
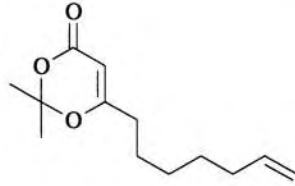
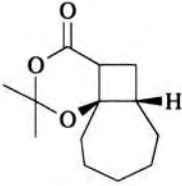
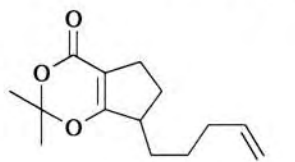
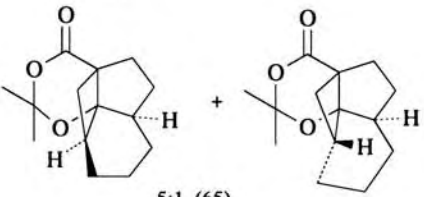
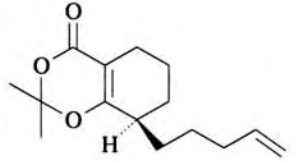
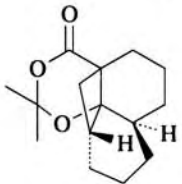
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		Pyrex, CH ₃ CN:acetone, 9:1	 (81)	121
C ₁₃		Pyrex, CH ₃ CN:acetone, 9:1	 (57)	121
C ₁₄		Pyrex, CH ₃ CN:acetone, 9:1, 0°, 4 h	 5:1 (65)	429
C ₁₅		Pyrex, CH ₃ CN:acetone, 9:1, 0°, 4 h	 (88)	131, 430

TABLE XXXII. 3-ALKENYLDIOXOLENONES (Continued)

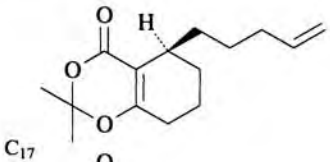
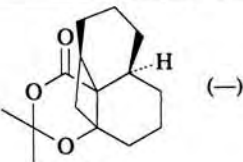
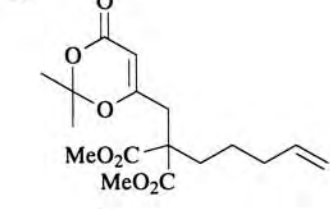
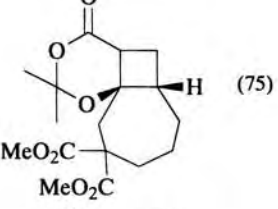
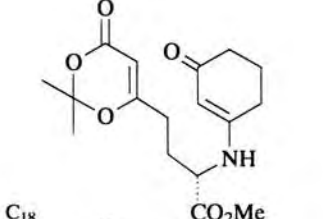
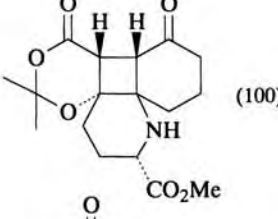
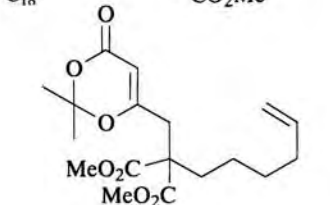
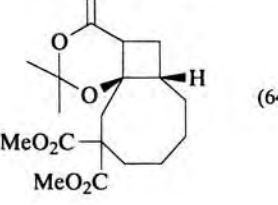
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, CH ₃ CN:acetone, 9:1	 (—)	430
	Pyrex, CH ₃ CN:acetone, 9:1	 (75)	121
	Pyrex, CH ₃ CN, 0, 75 min	 (100)	118, 143
	Pyrex, CH ₃ CN:acetone, 9:1	 (64)	121

TABLE XXXII. 3-ALKENYLDIOXOLENONES (Continued)

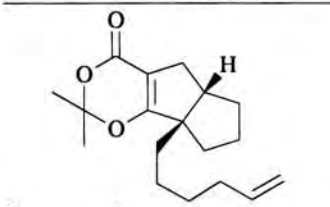
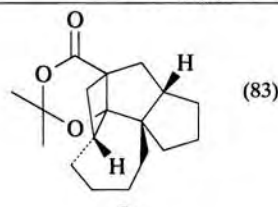
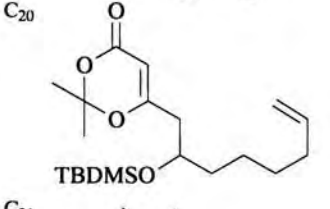
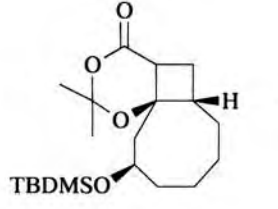
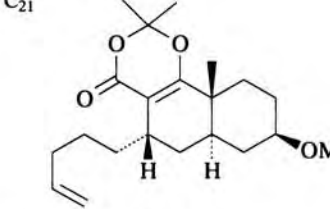
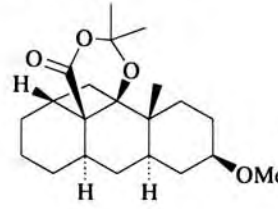
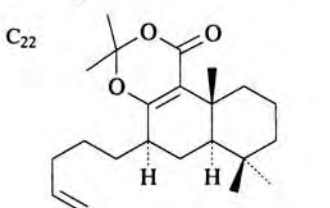
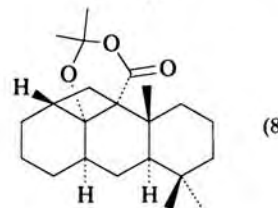
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, CH ₃ CN:acetone, 9:1, 0°, 90 min	 (83)	132
	Pyrex, CH ₃ CN:acetone, 9:1	 4:1 β:α (55)	121
	Pyrex, CH ₃ CN:acetone, 9:1	 (77)	431
	Pyrex, CH ₃ CN:acetone, 9:1	 (85)	432

TABLE XXXIII. 4-ALKENYLBUTENOLIDES

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	—	 (45)	433
C ₁₂ 	Quartz, acetone	 (77)	112, 328
C ₁₃ 	Quartz, acetone	 (33) + (7) + (16)	112, 328
	Quartz, acetone	 (34)	112, 328

TABLE XXXIII. 4-ALKENYLBUTENOLIDES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Quartz, acetone	 (66)	112, 328
C ₁₆ 	Quartz, <i>p</i> -xylene, 45 min	 (88)	433
	Quartz, acetone	 (66)	433
C ₁₇ 	Quartz, <i>p</i> -xylene	 (86)	433

TABLE XXXIII. 4-ALKENYLBUTENOLIDES (Continued)

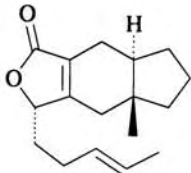
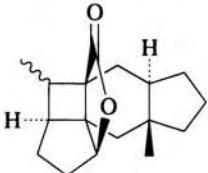
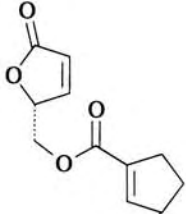
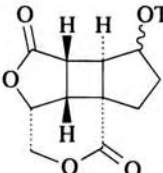
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Quartz, <i>p</i> -xylene	 (86)	433
 TBDMSO	CH ₃ CN	 (61)	115

TABLE XXXIV. MISCELLANEOUS NITROGEN CONTAINING CYCLIC ENONES

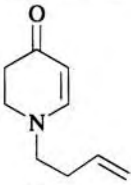
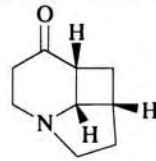
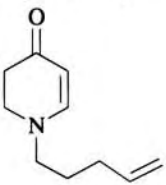
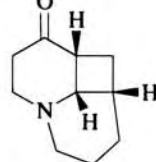
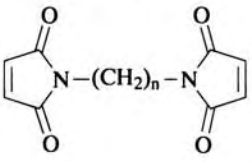
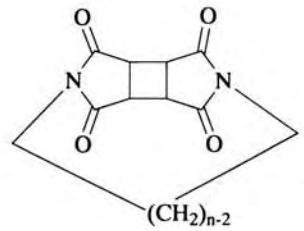
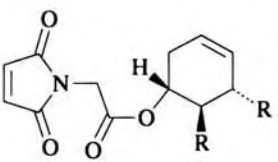
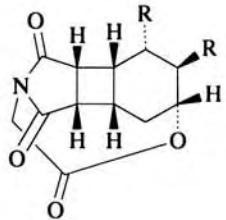
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₉ 	Pyrex, CH ₃ CN, 1.5 h	 (56)	334
C ₁₀ 	Pyrex, CH ₃ CN, 5 h	 (48)	334
	CH ₃ CN or CH ₂ Cl ₂	 n 3 (100) 4 (85) 5 (98) 6 (95) 7 (80)	434
C ₁₂ 	Pyrex, acetone	 R = H (51) R = Me (37)	148

TABLE XXXV. ALKENYPYRIMIDINES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₂		>300 nm, 25°	(74)	435
		>290 nm	(68)	435
C ₁₃		254 nm, H ₂ O	R = H (80) R = Me (90)	436
C ₁₄		Pyrex, CH ₃ CN, acetone, 11 h	(65)	148

TABLE XXXVI. ALKENYLBENZOPYRANONES

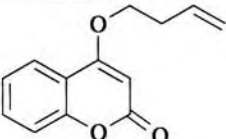
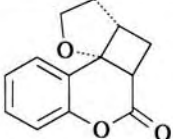
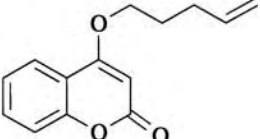
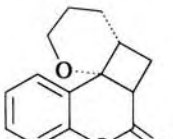
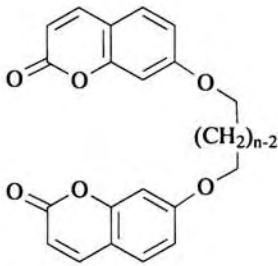
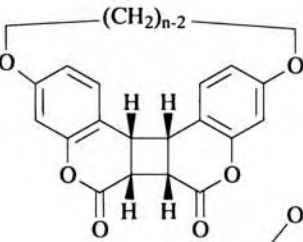
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₃ 	Pyrex, benzene	 (63)	116
C ₁₄ 	Pyrex, benzene	 (—)	116
C ₂₀ C ₂₁ C ₂₃ C ₂₇ 	—	 I + II I:II n = 2, 85:15 (—) n = 3, 41:49 (—) n = 5, 40:60 (—) n = 9, 33:67 (—)	437

TABLE XXXVII. ALKENYLBENZOLACTAMS

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																		
	350 nm		338																		
C ₉ C ₁₀		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>(45)</td> </tr> <tr> <td>Cl</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>OMe</td> <td>(70)</td> </tr> </tbody> </table>	R ¹	R ²		Cl	H	(—)	OMe	H	(45)	Cl	OMe	(—)	H	OMe	(—)	OMe	OMe	(70)	
R ¹	R ²																				
Cl	H	(—)																			
OMe	H	(45)																			
Cl	OMe	(—)																			
H	OMe	(—)																			
OMe	OMe	(70)																			
C ₁₁	350 nm		338																		
C ₁₀ C ₁₁		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>OMe</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²		Cl	H	(—)	OMe	H	(—)	Cl	OMe	(—)	H	OMe	(—)	OMe	OMe	(—)	
R ¹	R ²																				
Cl	H	(—)																			
OMe	H	(—)																			
Cl	OMe	(—)																			
H	OMe	(—)																			
OMe	OMe	(—)																			
C ₁₂		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th></th> </tr> </thead> <tbody> <tr> <td>Cl</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>Cl</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>OMe</td> <td>(—)</td> </tr> <tr> <td>OMe</td> <td>OMe</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²		Cl	H	(—)	OMe	H	(—)	Cl	OMe	(—)	H	OMe	(—)	OMe	OMe	(—)	
R ¹	R ²																				
Cl	H	(—)																			
OMe	H	(—)																			
Cl	OMe	(—)																			
H	OMe	(—)																			
OMe	OMe	(—)																			

TABLE XXXVII. ALKENYLBENZOLACTAMS (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																														
	Pyrex		119																														
C ₁₂ C ₁₃		<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>R⁴</th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>H</td> <td>H</td> <td>(93)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>H</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>H</td> <td>Me</td> <td>H</td> <td>(—)</td> </tr> <tr> <td>H</td> <td>H</td> <td>H</td> <td>Me</td> <td>(—)</td> </tr> </tbody> </table>	R ¹	R ²	R ³	R ⁴		H	H	H	H	(93)	Me	H	H	H	(—)	H	Me	H	H	(—)	H	H	Me	H	(—)	H	H	H	Me	(—)	
R ¹	R ²	R ³	R ⁴																														
H	H	H	H	(93)																													
Me	H	H	H	(—)																													
H	Me	H	H	(—)																													
H	H	Me	H	(—)																													
H	H	H	Me	(—)																													
	350 nm, CH ₃ OH		(32) 338																														
	CH ₃ OH		1:7 (81) 119																														

TABLE XXXVII. ALKENYLBENZOLACTAMS (Continued)

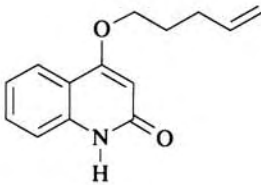
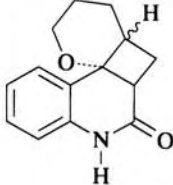
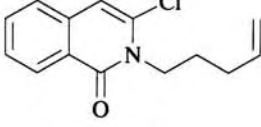
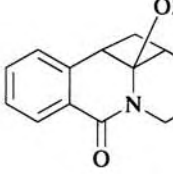
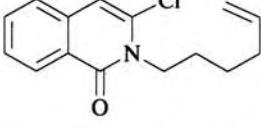
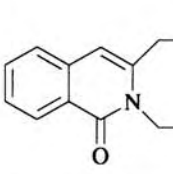
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₄ 	CH ₃ OH	 (—)	119
	350 nm, CH ₃ OH	 (57)	338
C ₁₅ 	350 nm, CH ₃ OH	 (—)	338

TABLE XXXVIII. 1,5-HEXADIEN-3-ONES

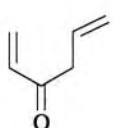

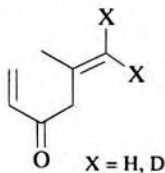
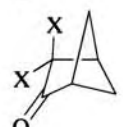
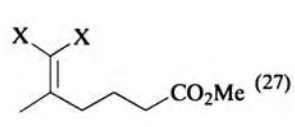
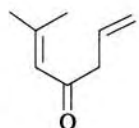

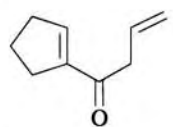
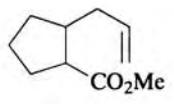
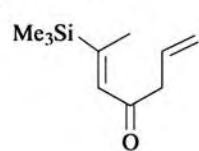
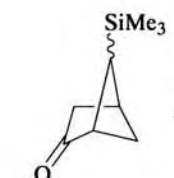
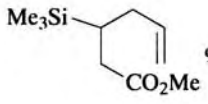
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₆ 	>340 nm, benzene, CH ₃ OH	 (70-90)	102, 105, 438, 101, 439, 440
C ₇  X = H, D	>340 nm, benzene, CH ₃ OH	 (43) +  (27)	101, 012, 105, 438, 441
C ₈ 	>340 nm	 (>95)	101, 105
C ₉ 	>340 nm	 (100)	105
C ₁₀ 	>340 nm, benzene, CH ₃ OH	 +  94:6 (70-90)	102, 438

TABLE XXXVIII. 1,5-HEXADIEN-3-ONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	>340 nm	(0) + (100)	105
	>340 nm, benzene, CH ₃ OH	(70-90)	102, 438
	>340 nm	(9) + (82)	101, 105
	—	(H) + 93:7 (70-90)	102, 105, 438
	—	(7) + (41) + (14)	105

TABLE XXXVIII. 1,5-HEXADIEN-3-ONES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	>340 nm, benzene, CH ₃ OH	+ (70-90)	102, 438
	Pyrex, 15-30°	(H) R = Me (78) R = CH ₂ Ph (92)	122, 123, 390
	—	(R) R = H (63) R = Ph (58)	442

568

569

TABLE XXXIX. 1-ACYL-1,5-HEXADIENES

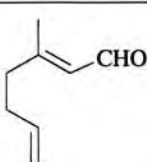
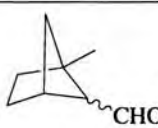
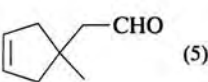
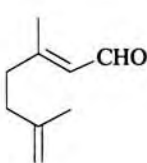

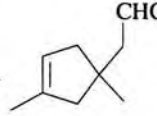
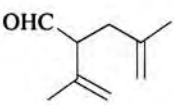
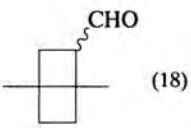
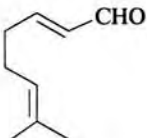
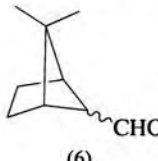
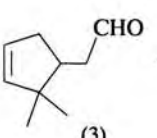
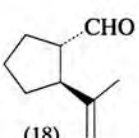
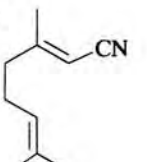
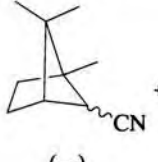
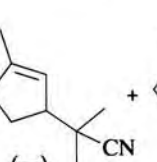
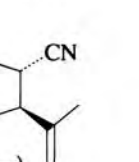
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ 	Pyrex, benzene	 (14) +  (5)	443
C ₉ 	Pyrex, benzene	 (5) +  (7) +  (30) +  (18)	365
	Pyrex, benzene	 (6) +  (3) +  (18)	443
C ₁₀ 	Pyrex, benzene, PhCOEt	 (6) +  (3) +  (18)	443

TABLE XXXIX. 1-ACYL-1,5-HEXADIENES (Continued)

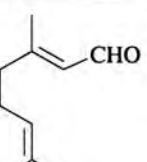
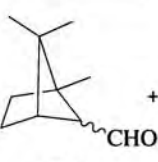
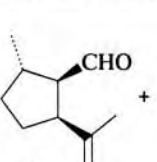
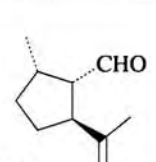
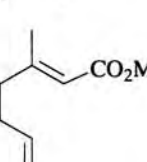
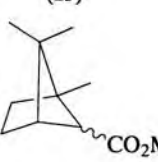
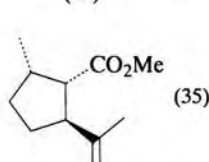
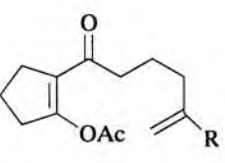
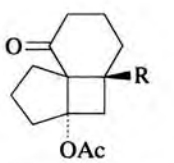
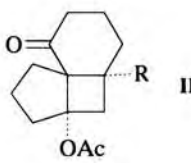
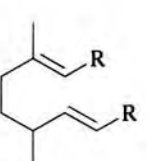
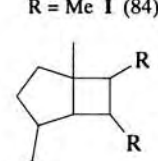
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
	Pyrex, benzene	 (25) +  (5) +  (42)	105, 443, 444, 445, 446
C ₁₁ 	Pyrex, benzene, PhCOEt	 (18) +  (35)	443
	Pyrex, EtOAc	 I +  II	124
C ₁₃	Pyrex, EtOAc	R = H I (87) + II (0.7)	124
C ₁₄	Pyrex, EtOAc	R = Me I (84) + II (2.5)	124
	Pyrex, PhCOCH ₃ , EtOH, 48 h	 (53)	124
C ₁₅		R = COMe (53)	
C ₁₇		R = CO ₂ Et (—)	

TABLE XL. 2-ACYL-1,5-HEXADIENES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₈ C ₉		>340 nm >340 nm	 R = H (80) R = Me (12)	365 365
C ₁₁		Pyrex, benzene	(28)	443
C ₁₁		Pyrex, pentane, -20°	(—)	365
C ₁₄		Pentane, 1 week	(67)	447

TABLE XLI. 1,6-HEPTADIEN-3-ONES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.																											
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>Yield(s) (%)</th> </tr> </thead> <tbody> <tr> <td>H</td> <td>H</td> <td>60:40 (95)</td> </tr> <tr> <td>H</td> <td>Me</td> <td>90:10 (93)</td> </tr> <tr> <td>Me</td> <td>H</td> <td>65:35 (71)</td> </tr> <tr> <td>OAc</td> <td>H</td> <td>43:57 (—)</td> </tr> <tr> <td>OAc</td> <td>H</td> <td>20:80 (—)</td> </tr> <tr> <td>OAc</td> <td>H</td> <td>11:89 (82)</td> </tr> <tr> <td>OAc</td> <td>H</td> <td>48:52 (—)</td> </tr> <tr> <td>OAc</td> <td>H</td> <td>60:40 (93)</td> </tr> </tbody> </table>	R ¹	R ²	Yield(s) (%)	H	H	60:40 (95)	H	Me	90:10 (93)	Me	H	65:35 (71)	OAc	H	43:57 (—)	OAc	H	20:80 (—)	OAc	H	11:89 (82)	OAc	H	48:52 (—)	OAc	H	60:40 (93)	
R ¹	R ²	Yield(s) (%)																													
H	H	60:40 (95)																													
H	Me	90:10 (93)																													
Me	H	65:35 (71)																													
OAc	H	43:57 (—)																													
OAc	H	20:80 (—)																													
OAc	H	11:89 (82)																													
OAc	H	48:52 (—)																													
OAc	H	60:40 (93)																													
C ₁₀		Uranium glass, hexanes		366																											
C ₁₁		Uranium glass, hexanes		366																											
		Uranium glass, hexanes		366																											
C ₁₂		Pyrex, CH ₃ CN, 5-10°		106,107																											
		Pyrex, acetone, -70°		106,107																											
		Pyrex, ether, -70°, 40 h		106,107																											
		Pyrex, CH ₃ CN, 65°		106,107																											
		Pyrex, hexane		390,391																											
			R = H II:III:IV = 33:52:5	366																											
C ₁₃		Uranium glass, hexane	R = Me I:II:III:IV = 8:20:42:18	366																											

TABLE XLI. 1,6-HEPTADIEN-3-ONES (Continued)

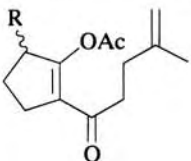
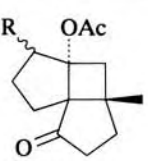
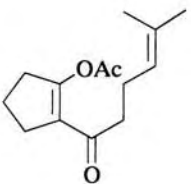
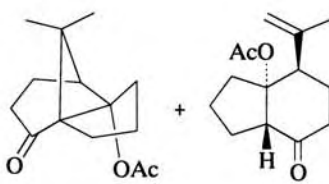
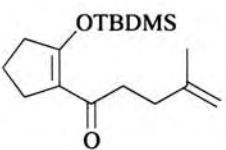
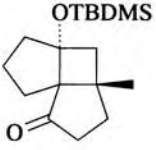
	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
				
		Pyrex, acetone, 40 h Pyrex, acetone, 5-10°, 60 h	R = H (82) R = Me (88)	107,160 448
C ₁₄				
		Pyrex, hexane, 5-10° Pyrex, acetone, -70°	42:58 (—) 17:83 (—)	106 106
C ₁₇			 (68)	106, 107 449

TABLE XLII. 3-AZA-1,5-HEXADIENES

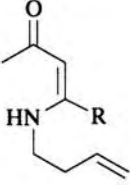
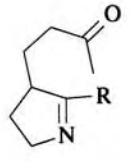
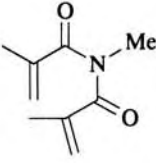
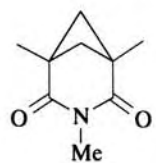
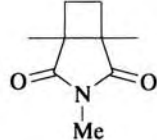
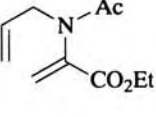
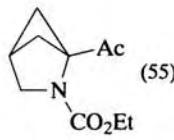
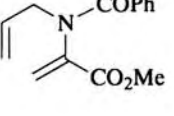
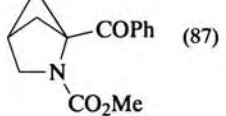
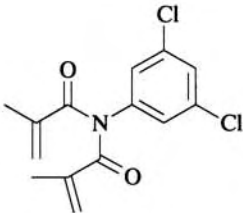
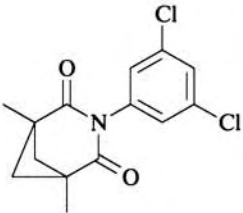
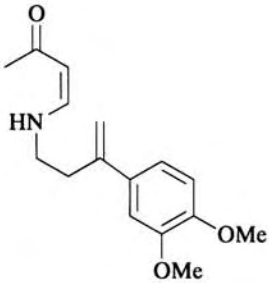
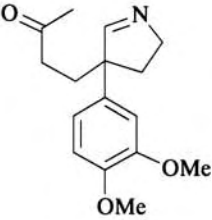
Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 C ₈ C ₉	Pyrex, CH ₃ CN	 R = H (70) R = Me (80)	450, 451
 C ₁₀	254 nm, CH ₃ CN	 (66) +  (7)	452
 C ₁₀	300 nm, acetone	 (55)	453
 C ₁₄	Benzene, Ph ₂ CO, 10 h	 (87)	454, 455

TABLE XLII. 3-AZA-1,5-HEXADIENES (Continued)

Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
 <chem>CC1=CC=C(C=C1)N(C2=CC=C(C=C2)Cl)C=C(C)C=C</chem>	254 nm, CH ₃ CN	 (37)	452
 <chem>CC1=CC=C(C=C1)N(C2=CC(OC)=C(OC)C=C2)C=C(C)C=C</chem>	Pyrex, CH ₃ CN	 (74)	450

C₁₆

TABLE XLIII. MISCELLANEOUS OXYGEN CONTAINING ENONES

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₁₆ C ₁₇		CH ₂ Cl ₂ , Ph ₂ CO		456
C ₂₉ C ₃₀		Pyrex, CH ₃ CN, 1 h Pyrex, CH ₃ CN, 1 h		n = 3 (—) n = 4 (—) n = 1 (18) n = 2 (71) 457 457
C ₃₂		Pyrex, CH ₃ CN, 1.5 h Pyrex, CH ₃ CN, 1.5 h		n = 1 (92) n = 3 (32) 458 458

TABLE XLIII. MISCELLANEOUS OXYGEN CONTAINING ENONES (Continued)

	Reactant	Reaction Conditions	Product(s) and Yield(s) (%)	Refs.
C ₄₂		300 nm, ether	R = $-(CH_2)_3-$ (32)	459
C ₄₄		350 nm, Ph ₂ CO, ether	R = $-CH_2CH_2OCH_2CH_2-$ (40-50)	460
C ₄₈		350 nm, Ph ₂ CO, acetone	R = $-CH_2(CH_2OCH_2)_2CH_2-$ (40-50)	460
C ₅₆		350 nm, Ph ₂ CO, ether	R = $-(CH_2)_{10}-$ (40-50)	460
C ₆₀		350 nm, Ph ₂ CO, toluene	R = $-(CH_2)_{12}-$ (40-50)	460

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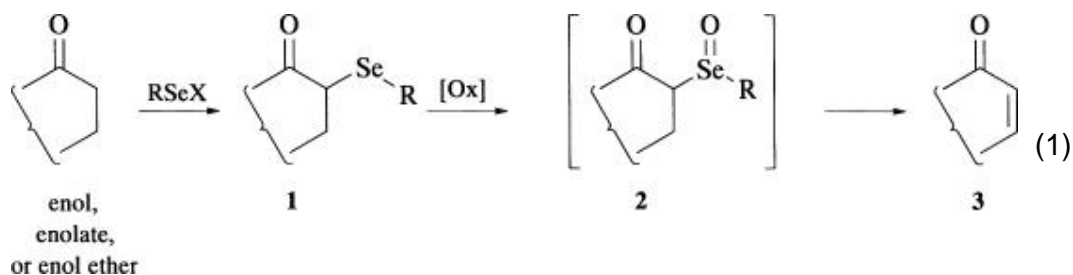
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Preparation of α, β -Unsaturated Carbonyl Compounds and Nitriles by Selenoxide Elimination

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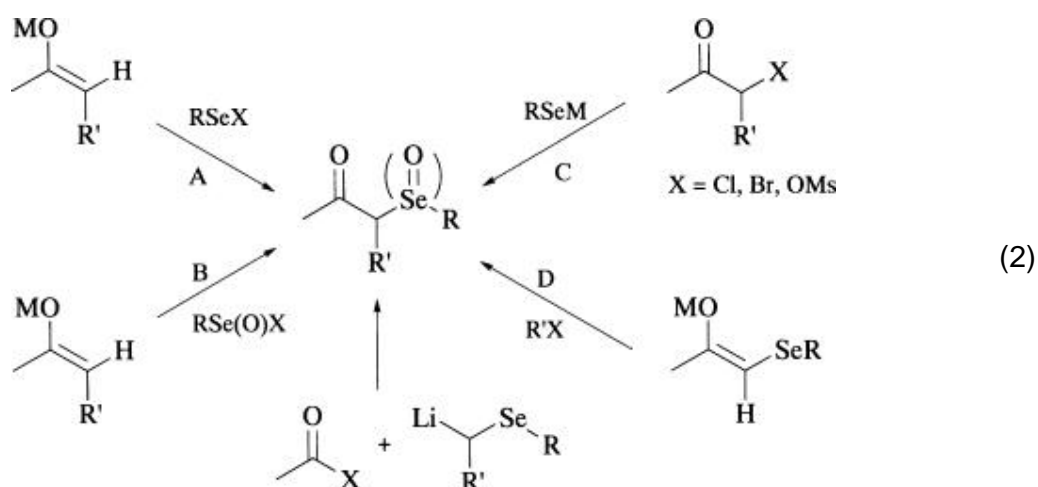
1. Introduction

Hydrogenation and dehydrogenation reactions play a key role in synthetic organic chemistry. The discoveries that selenium and sulfur substituents could be easily introduced α to a variety of acidifying functional groups, and that these derivatives could be smoothly converted to olefins by selenoxide (1-4) or sulfoxide (5, 6) *syn* elimination under mild conditions greatly broadened the range of α, β -unsaturated carbonyl compounds that could be prepared from their saturated analogs. This chapter covers the preparation from enols or enolates of α -RSe substituted carbonyl compounds (1) and nitriles and their conversion to olefins 3 by thermolysis of the derived selenoxides 2 (Eq. 1). Other procedures for preparing 1 or 2 are discussed in a limited way, and they are included in the tables, but the two-step dehydrogenation of Eq. 1 is by far the most frequently used.



The rapid acceptance of the selenoxide elimination as a synthetic procedure was the result of two factors: the ease with which many organoselenium compounds could be prepared using readily available, powerful electrophilic and nucleophilic selenium reagents, and the mild conditions (-50° to 40°) under which selenoxides fragment to olefins. Recognized selenoxide eliminations to form olefins were reported in 1967 (7) and 1970, 8,8a well after the related sulfoxide eliminations had been studied extensively. The application of the sulfoxide (5) and selenoxide (1-4) eliminations according to Eq. 1 were reported almost simultaneously by several groups in 1973. These reactions have been the subject of several reviews. (9-12) The principal

procedures and reagents for the preparation of the requisite selenium compounds were also identified at that point (Eq. 2).



Method A: Reaction of enolates, enols, enol ethers, and enamines with benzeneselenenyl chloride or bromide, or diphenyl diselenide. (1, 3, 4, 13)

Method B: Reaction of enols with seleninylating agents $[\text{C}_6\text{H}_5\text{Se}(\text{O})\text{Cl}]$, $(\text{C}_6\text{H}_5\text{SeO})_2\text{O}$. (2, 14)

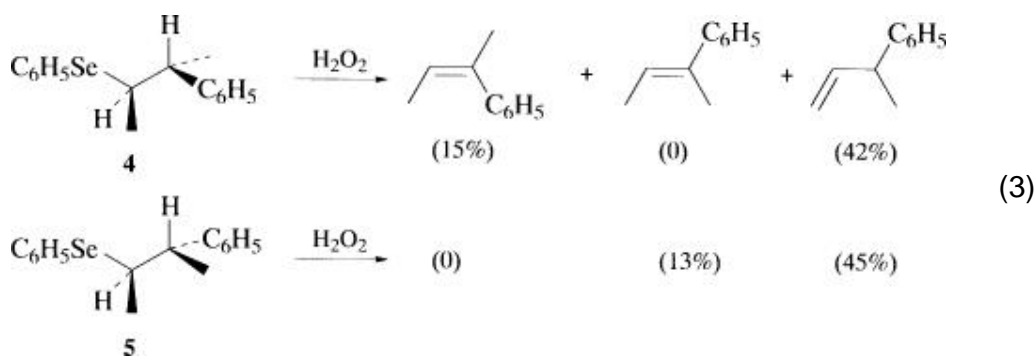
Method C: Nucleophilic substitution of α -halo carbonyl compounds with metal selenolates. (3)

Method D: Alkylation of α -phenylseleno carbonyl compounds (3, 15) and acylation of α -lithio selenides or selenoxides. (16, 17)

2. Mechanism and Stereochemistry

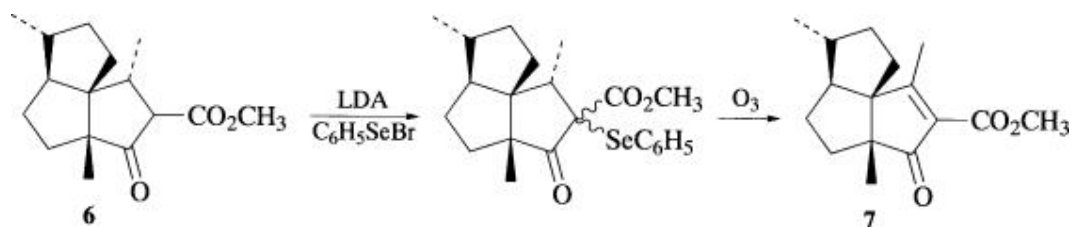
2.1. *syn* Elimination

The selenoxide elimination has been the subject of little detailed mechanistic work. (18) The reaction has the characteristics of a *syn* elimination. Thus the diastereomeric selenides **4** and **5** produce the expected olefins (Eq. 3). (19) Regiochemistry in cyclic systems can be decisively controlled by taking advantage of the required *syn* relationship between selenium and the β proton. This method of regiocontrol has been particularly important in the area of α -methylenelactone synthesis. (15, 20)



The behavior of selenoxides when a *cis* β hydrogen is not available depends on the possibility of equilibration. If there is an exchangeable hydrogen at the α position, the selenoxide may equilibrate (weakly basic conditions are beneficial (21)), and good yields of olefin can sometimes be obtained provided there is a *trans* β hydrogen. (22, 23) In other cases, selenoxides lacking a *cis* β hydrogen fail to give good yields of enone. (23, 24) In cases where equilibration is not possible only one isomer can eliminate. The last operation in a synthesis of methyl cantabrenonate, (25) the selenation—oxidation of the β -keto ester **6**, is illustrative. A 1:1 mixture of isomeric selenides is formed on treatment of the enolate with benzeneselenenyl bromide and only one of the isomers can be converted to enone **7** in good yield. The other isomer is recycled by deselenation with sodium benzeneselenolate.

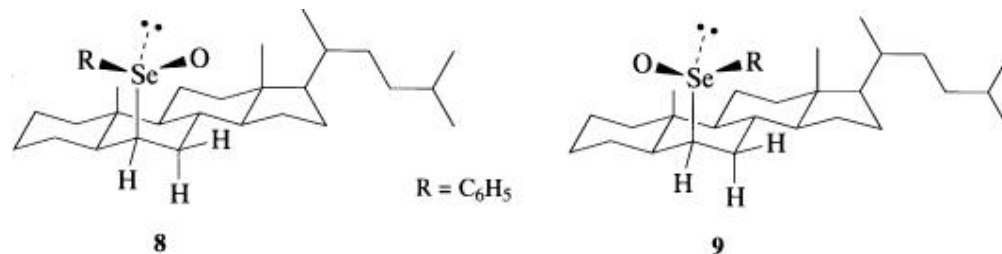
The selenoxide elimination responds to structural effects in the same way as does the better-known sulfoxide elimination. Thus formation of conjugated double bonds proceeds at lower temperatures than the formation of isolated double bonds.



The effect is especially large for formation of α , β -unsaturated carbonyl compounds, where it has been ascribed to dipole repulsions between the polar carbonyl and selenoxide or sulfoxide groups. (26) Detailed work on the selenoxide elimination has been hampered by the fact that almost all keto selenoxides decompose well below room temperature. (27)

2.2. Stereochemistry at Selenium

Eliminations are frequently conducted on mixtures of diastereomeric selenoxides, yet almost nothing is known about how the stereochemistry at the stereogenic selenium atom affects the rate and regioselectivity of selenoxide eliminations. In a key early study, the steroid selenoxides **8** and **9** were separated by low temperature chromatography, and their structures assigned by comparison of CD spectra with sulfur analogs. Compound **8** fragments at 0°; the isomer **9**, which cannot easily



reach the appropriate conformation needed for *syn* elimination, is stable to 5°. (8) However, the epimerization of selenoxides is acid-catalyzed and most selenoxides readily epimerize at selenium. (28-30) Thus, selenoxide epimers may be equilibrating during selenoxide eliminations not specifically buffered with weak base.

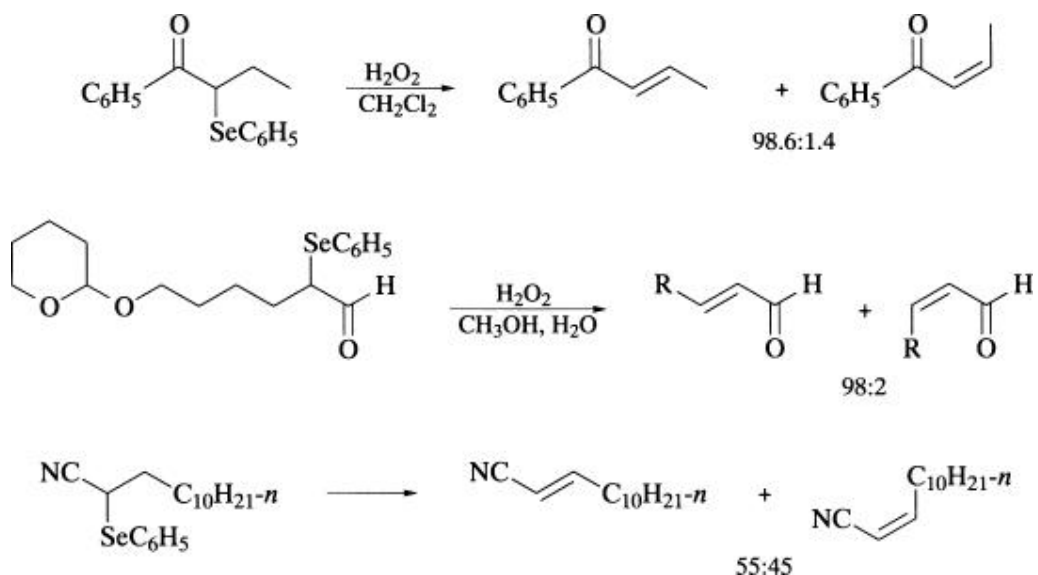
2.3. Olefin Stereochemistry

The selenoxide elimination gives modest selectivity for the formation of simple *trans* olefins when these are unstrained. *Trans/cis* ratios are similar to those given by other *syn* eliminations.

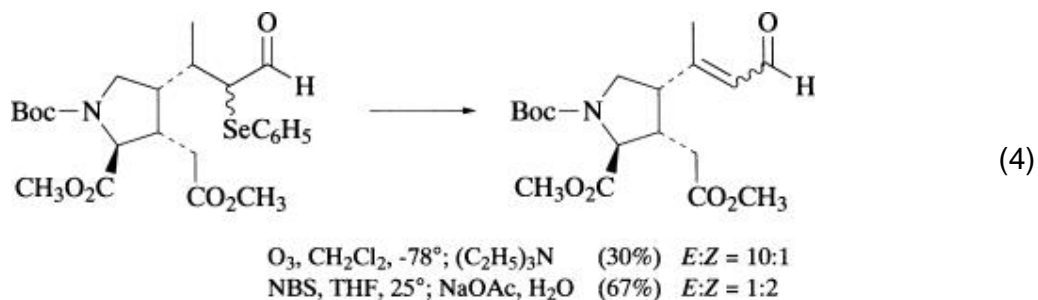
sec-Butyl-X	1-Butene	<i>trans</i>-2-Butene	<i>cis</i>-2-Butene	Ref.
X = C ₆ H ₅ Se(O)	61%	28%	11%	19

C ₆ H ₅ S(O)	60%	25%	15%	31
(CH ₃) ₂ N(O)	67%	21%	12%	32
CH ₃ CO ₂	57%	28%	15%	33

However, when α , β -unsaturated ketones, amides, (34) or esters are formed, the *trans* isomer is the only one detected, although detection limits have rarely been reported. For butyrophenone and even a straight-chain aldehyde the selectivity is 98% or better. (35, 36) α , β -Unsaturated nitriles are formed with much lower *trans* selectivity. (37, 38)

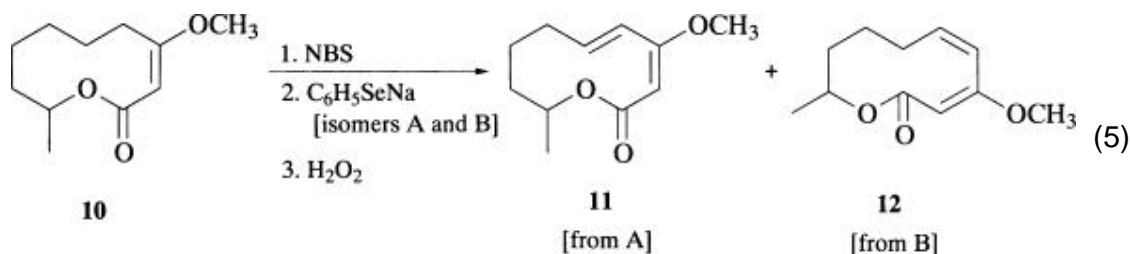


The olefin *E/Z* ratio in stereochemically complex systems can be affected by the method used to carry out the selenoxide elimination. In Eq. 4 two procedures for



performing the oxidation resulted in a preponderance of opposite isomers of an α , β -unsaturated aldehyde. (39) It is not known whether the change in stereochemistry results from effects of diastereomeric ratios at carbon and/or selenium, or from some other factor.

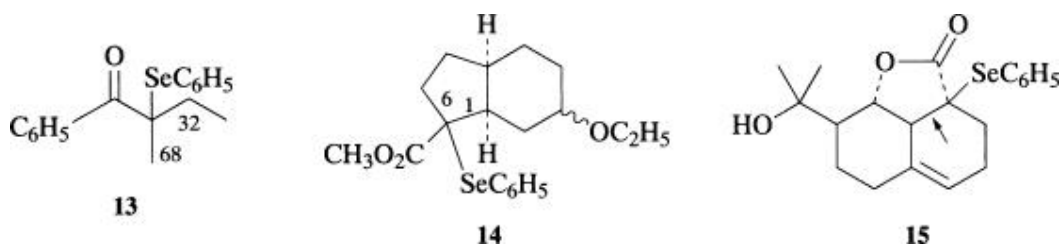
In medium ring compounds, selenides stereoisomeric at carbon can give double bond isomers. The free radical bromination of the lactone **10** in Eq. 5 gives two stereoisomers, which are in turn converted to isomeric selenides. One selenide gives only *cis* olefin **11**, the other only *trans* **12**. (40)



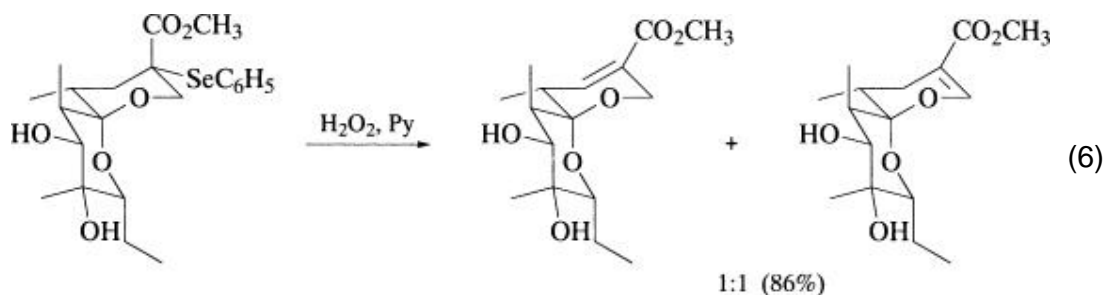
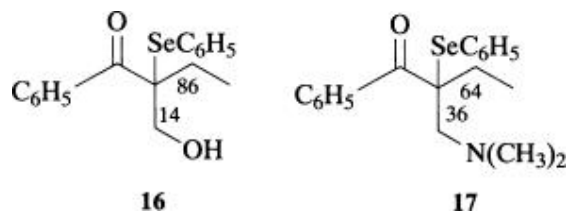
2.4. Regiochemistry of the Selenoxide Elimination

The factors that control the regioselectivity of selenoxide eliminations have not been studied systematically. Some general trends are clear however (the numbers on the structures below are product ratios of isomeric olefins):

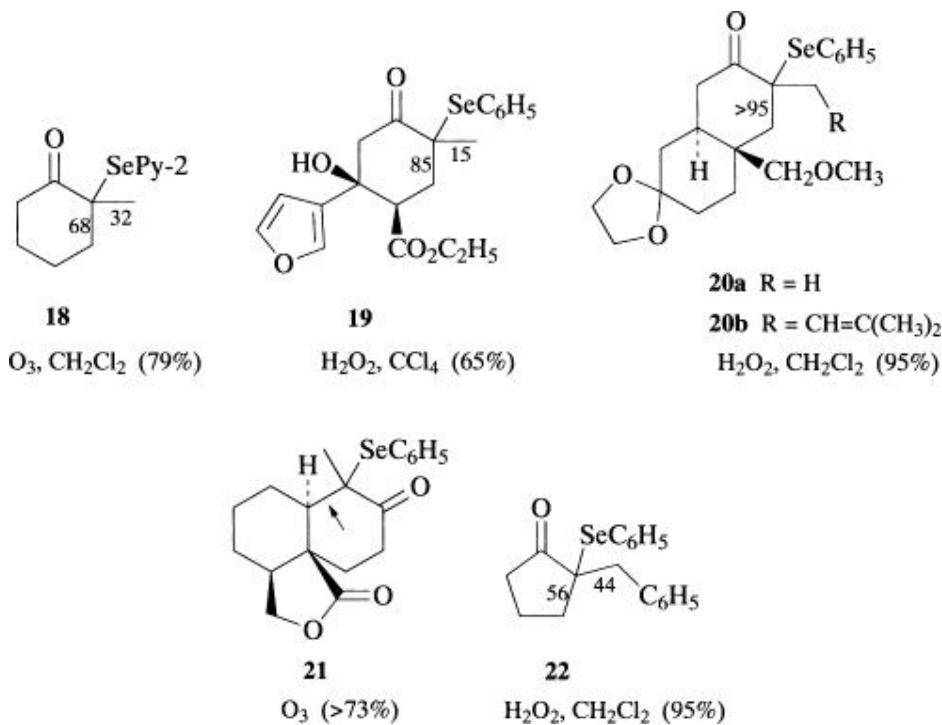
- a. Other things being equal, elimination toward the less substituted carbon is favored, but not by an overwhelming amount. The trend is seen in acyclic compounds such as **13**, (41) as well as cyclic compounds such as **14**. (42)



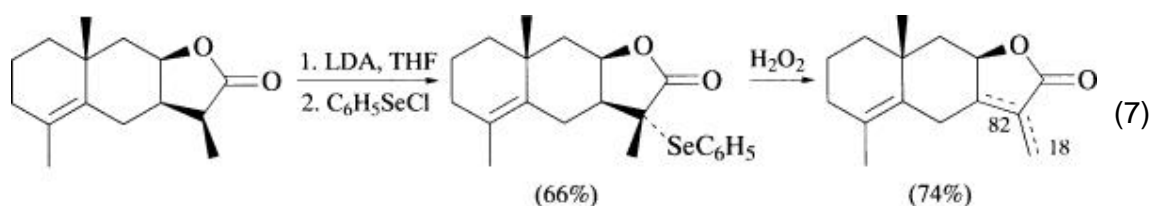
- b. Elimination to form conjugated double bonds is favored (e.g., **15**). This feature is shared by virtually all elimination reactions. (43)
- c. Elimination toward oxygen (**16**) and, to a lesser extent, nitrogen (**17**) substituents is disfavored, (41) although there are exceptions (Eq. 6). (44) The effect is not as large for selenides with an α carbonyl group as it is for simple alkyl selenides (formation of allyl alcohols rather than enols). (17, 45) Rationalizations on the basis of dipole effects (26) and the π -donor properties of the substituent have been presented. (46)



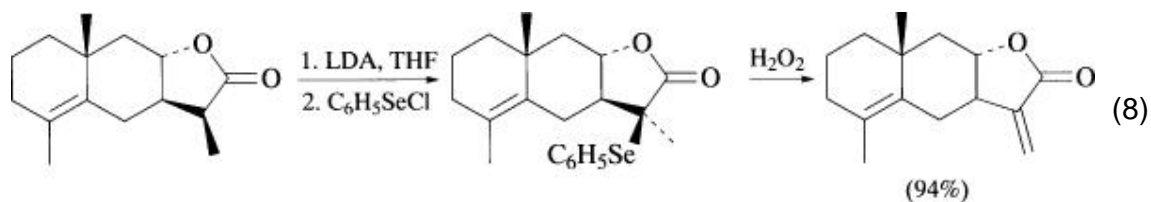
- d. Elimination to form endocyclic olefins is usually favored over exocyclic elimination in 5- and 6-membered rings unless there is no *syn* hydrogen. Because such systems are conformationally constrained, it is likely that one significant factor is the (invariably unknown) effect of stereochemistry at selenium.
- 2-Methylcyclo-hexanones give predominantly (18, (47) 19 (48)) or exclusively (20a, (49) 21 (50)) the endocyclic product. Even when exocyclic elimination produces a conjugated double bond, the major product is often the endocyclic olefin (20b, (51) 22 (52)) if a *cis* hydrogen is available.



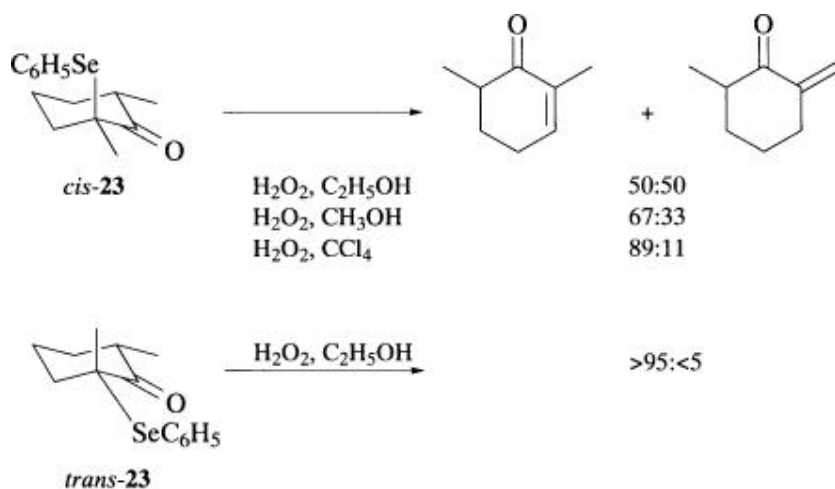
Considerable work has been done on α -alkylated γ -lactones. (15, 20) These also produce largely endocyclic butenolides if a *syn* hydrogen is available. Good regio-control can often be achieved by appropriate choice of synthetic procedure for preparation of the α -phenylseleno- α -methyl lactone. Thus selenenylation and oxidation of a *cis*-fused lactone produces endocyclic olefin as the major product (Eq. 7). (20)



The related *trans*-fused γ -lactone produces only exocyclic olefin, since the intermediate selenide lacks a *cis* ring hydrogen (Eq. 8). (20) Reversing the order of introduction of methyl and selenide groups leads to the opposite stereochemical relationship.



Some of the factors that control the regioselectivity are suggested by the results with compounds *cis*-**23** and *trans*-**23**. The stereochemistry at selenium probably plays little role for *trans*-**23**, with its equatorial selenide and selenoxide group, and the inherent preference for endocyclic elimination is seen. For *cis*-**23**, one of the diastereomeric selenoxides should prefer to form the exocyclic enone (see discussion

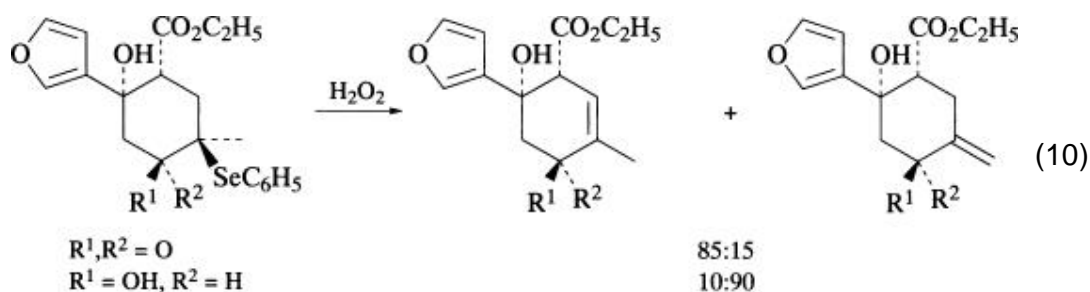
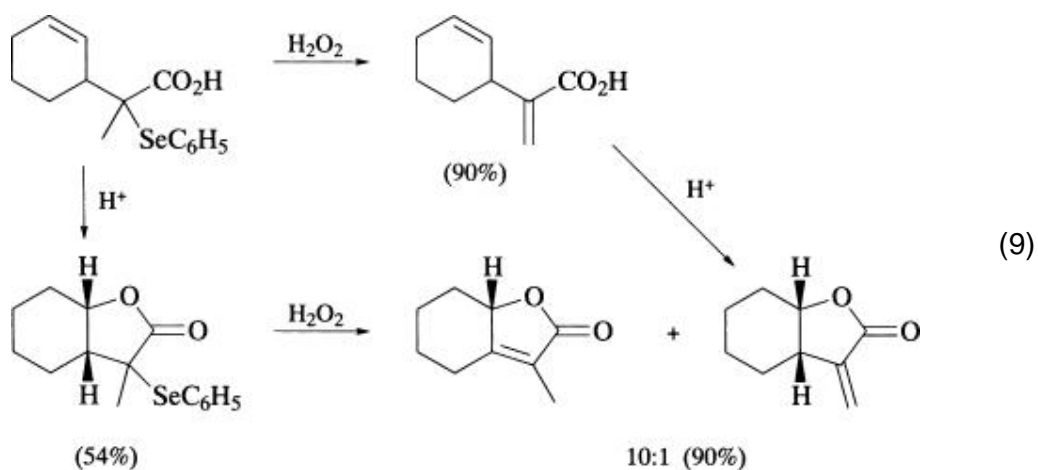


of compounds **8** and **9** (8)) and the other endocyclic enone. The large effect of solvent may reflect either variability in the diastereoselectivities in the oxidation or different relative rates of selenoxide epimerization and *syn* elimination. Variations in the regiochemistry of selenoxide elimination of a β -hydroxy selenoxide have also been ascribed to stereochemical effects at selenium. (17) Unfortunately, no direct evidence concerning selenoxide stereochemistry is available for any carbonyl substituted system, so we can only speculate.

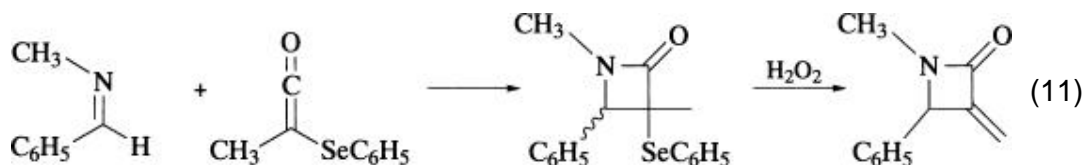
The endocyclic preference can be ascribed to dipole interactions between the selenoxide and carbonyl groups. (26) The effect should be especially strong

for selenoxides because of their strongly dipolar nature. This argument can also provide an alternative rationalization of the variability in exo vs. endocyclic elimination for *cis*-**23**. Polar solvents favor the more polar exocyclic elimination transition state.

Such well-defined dipole interactions are absent in acyclic selenides, and the normal preference for elimination toward less substituted carbon should be observed. In fact, there is an almost complete reversal of regiochemistry between selenoxide elimination (as well as sulfoxide elimination. (26)) in an acyclic acid and the derived lactone (Eq. 9). (53) The reversal in regioselectivity between a 2-methylcyclohexanone and the related cyclohexanol (Eq. 10) is also easily understood in these terms. (48)



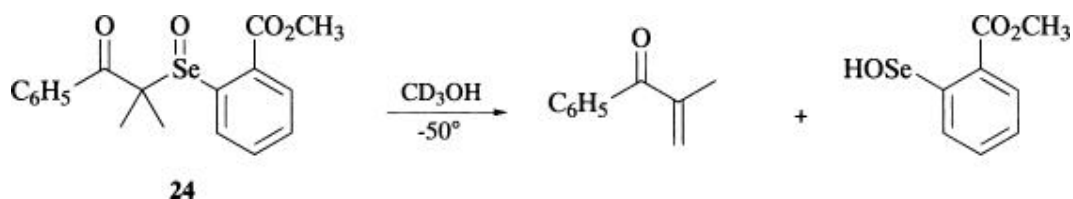
In several examples of four-membered ring lactams, elimination gives only the exocyclic double bond (Eq. 11). (54, 55) The selenides are mixtures of isomers but the



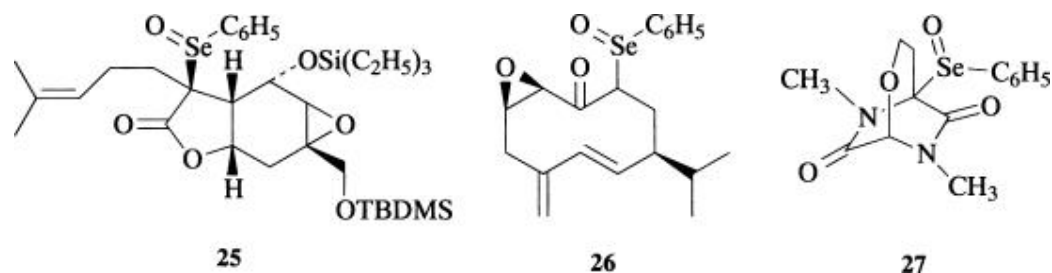
ratios were not reported, so it is unknown whether endocyclic elimination was a significant possibility.

2.5. Rate of the Selenoxide Elimination

Simple alkyl selenoxides eliminate with half-lives of a few minutes to several hours at room temperature. (27) Most keto selenoxides decompose at temperatures below 0°. For example, compound **24** has a $t_{1/2}$ of 13 minutes at -50° in methanol, (56) compared to a $t_{1/2}$ of 38 minutes at 38° in chloroform for isopropyl phenyl selenoxide. (27)



If the elimination produces a strained double bond or steric effects inhibit elimination, even carbonyl and cyano selenoxides may be stable at room temperature or higher. Examples are 1-phenylselenino-1-cyanocyclopropane, (57) and compounds **25**, (58) **26**, (59) and **27** (60) (see also Eq. 54). (35)



Selenoxide elimination rates also depend on the substituent on selenium. Electron withdrawing groups increase the rate; *p*-nitrophenyl ethyl selenoxide eliminates four times, *o*-nitrophenyl 24 times, and *p*-methoxyphenyl half as fast as does phenyl ethyl selenoxide. (27) Since eliminations of carbonyl substituted selenoxides are already very fast, there is little reason to use groups other than phenyl (pyridyl (47) and methyl (61, 62) have been used).

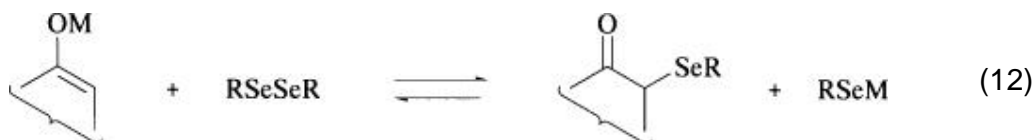
3. Scope and Limitations

3.1. Reagents for Introducing Seleno Groups

$(C_6H_5)_2Se_2$	Diphenyl diselenide (63)
$(C_5H_4N)_2Se_2$	2-Pyridyl diselenide (47)
C_6H_5SeCl	Benzeneselenenyl chloride (63)
C_5H_4NSeCl	2-Pyridineselenenyl chloride (47)
C_6H_5SeBr	Benzeneselenenyl bromide
C_5H_4NSeBr	2-Pyridineselenenyl bromide (47)
$C_6H_5SeOCOCF_3$	Benzeneselenenyl trifluoroacetate (63a)
$C_6H_5SeNR_2$	<i>N,N</i> -Dialkylbenzeneselenenamide (64, 65)
$C_6H_5SeNPhth$	<i>N</i> -(Phenylseleno)phthalimide (66-68)
$C_6H_5SeSe(CH_3)C_6H_5 \cdot BF_4$	Phenylselenomethylphenylselenonium fluoroborate ⁶⁹
$(C_6H_5SeO)_2O$	Benzeneseleninic anhydride (70, 71)
$C_6H_5SeO_2H$	Benzeneseleninic acid
$C_6H_5Se(O)Cl$	Benzeneseleninyl chloride (2)
$C_6H_5SeCl_3$	Phenylselenium trichloride (72)
C_6H_5SeNa	Sodium benzeneselenolate (3, 73-75)
$C_6H_5SeSiMe_3$	Trimethylsilyl phenyl selenide (76, 77)
$C_6H_5SeAlR_2$	Dialkylaluminum phenyl selenide (78)

3.1.1.1. Diselenides

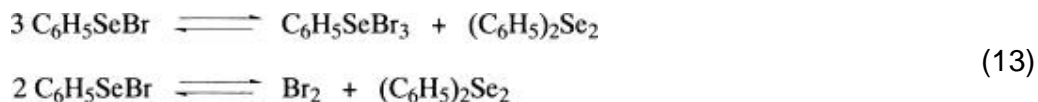
Diselenides are easily prepared, stable compounds which are the normal precursors to all of the other reagents listed above. They can themselves be used for electrophilic selenenylation of reactive enolates and carbanions. Enolate selenenylation is often reversible, and the position of the equilibrium of Eq. 12



depends on R and on the type of carbonyl compound. When R = C₆H₅ and M = Li, the equilibrium lies to the right for ester, lactone, and carboxylate enolates, and to the left for ketone and less basic enolates (e.g., β-dicarbonyl). For R = 2-pyridyl, it lies to the right for ketone enolates as well. (47) It has been possible to drive the reaction to the right by removing the byproduct RSeM produced during the reaction by oxidation with air. (58)

3.1.1.2. Selenenyl Halides

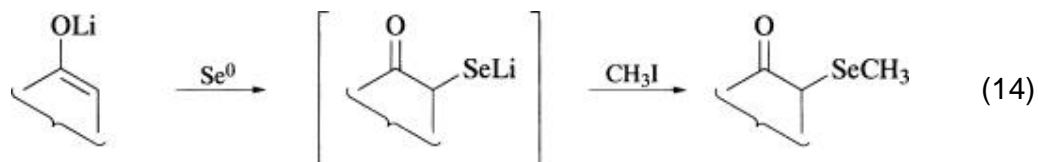
The most widely used electrophilic selenium reagents are the selenenyl halides. Benzeneselenenyl chloride is a shelf stable (but somewhat moisture sensitive) reagent, (63) which reacts rapidly with all classes of enolates, enols, and enol derivatives (enol acetates may require activation of the selenenyl chloride with silver salts. (2, 4)) Benzeneselenenyl bromide is usually prepared in situ by the stoichiometric reaction of bromine with diphenyl diselenide (1) since it is more difficult to crystallize than the chloride. Benzeneselenenyl bromide reacts well with enolates, but can behave as a brominating agent toward enols, perhaps through equilibria as in Eq. 13. Although these equilibria favor the selenenyl bromide, enough bromine or



phenylselenium tribromide may be present that under conditions of slow enolization the bromine can react preferentially. Thus, whereas benzeneselenenyl chloride reacts with ketones and aldehydes directly to introduce seleno groups, (3) the bromide usually gives α-bromination. (2) This is not the case for 2-pyridineselenenyl bromide, which selenenylates ketones and aldehydes (via their enols) in useful yields. (47)

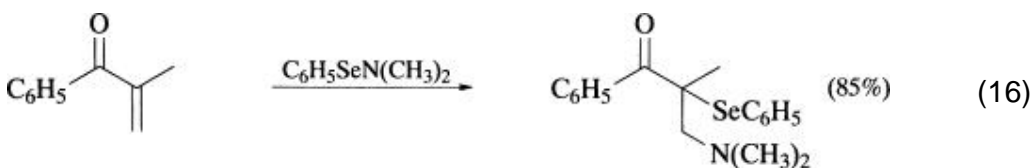
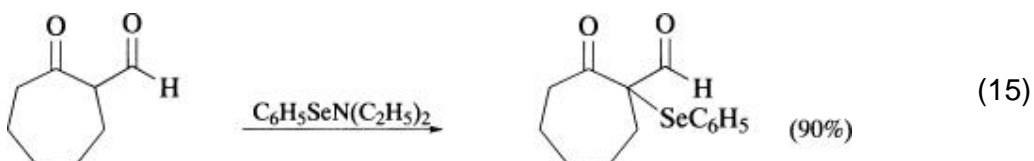
3.1.1.3. Elemental Selenium

An alternative to the use of organoselenium derivatives is the reaction of enolates with elemental selenium, followed by alkylation (Eq. 14). (61, 62) The procedure uses the least expensive source of selenium. Though it is widely used with organolithium and Grignard reagents for the preparation of selenolates and selenides, it has been infrequently used with enolates.



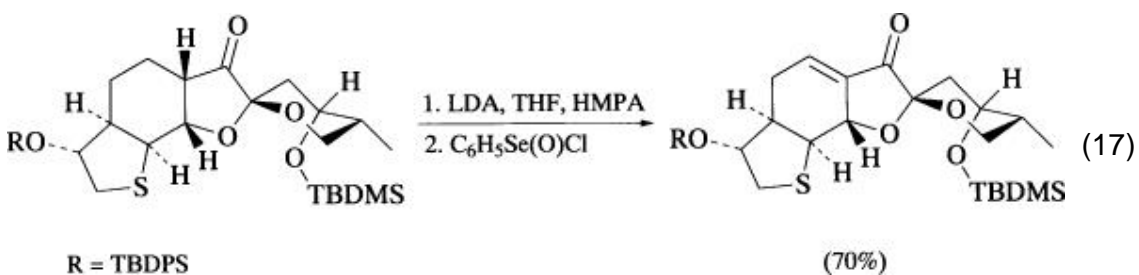
3.1.1.4. Selenenamides

These hydrolytically sensitive compounds can be used in several ways to introduce phenylseleno groups. With aldehydes (65, 79-82) and β -dicarbonyl compounds, (64) direct selenenylation occurs (Eq. 15). Unhindered enones and other reactive Michael acceptors undergo an interesting nucleophilic addition–intramolecular selenenylation sequence which produces β -amino selenides (Eq. 16). (83)



3.1.1.5. Benzeneseleninyl Chloride

The acid chloride of benzeneseleninic acid can be prepared by ozonation of benzeneselenenyl chloride. (2) Direct dehydrogenation can be accomplished by reaction of this reagent with enolates. It is quite moisture sensitive and yields are not exceptionally good, but it has found use when there are oxidatively sensitive functions in the molecule (Eq. 17). (84)



3.1.1.6. Benzeneseleninic Acid and Anhydride

Benzeneseleninic anhydride is prepared by oxidation (ozone) of diphenyl diselenide. It is shelf-stable, and not particularly hydrolytically sensitive. It has been used generally as a mild oxidant (hydroquinones and phenols to quinones, (85) amines to ketones and nitriles (70)). In the present context, benzeneseleninic anhydride has been extensively studied as a direct

dehydrogenating agent for ketones, (14) lactones, (86-89) oxazolines, (90) and lactams. (91)

3.1.1.7. Phenylselenium Trichloride

This reagent reacts with ketones to produce α -keto selenide dichlorides, which can be hydrolyzed to selenoxides. (72)

3.1.1.8. Diphenyl Diselenide with Oxidizing Agents

The use of diphenyl diselenide with oxidizing agents for direct dehydrogenation is not mechanistically well understood. Such systems include $\text{Ph}_2\text{Se}_2/\text{ArIO}_2$, (92) $\text{Ph}_2\text{Se}_2/\text{SeO}_2$, (93) and Ph_2Se_2 /electrochemical oxidation. (94) It is not clear whether reactions under these conditions involve direct formation of selenide or selenoxide intermediates (see below).

3.1.1.9. Selenolates and Other Nucleophilic Selenium Reagents

Alkali metal selenolates are usually prepared by reduction of diselenides. Sodium borohydride in solvents such as ethanol or dimethylformamide is commonly used. More potent reagents (i.e., not complexed to boron Lewis acids) are prepared by using dissolving metal reductions. (73)

A variety of other nucleophilic selenolate reagents such as PhSeSiMe_3 (77) and PhSeAlMe_2 (78, 95) have been prepared, but these are not commonly used for the synthesis of α -seleno carbonyl compounds.

3.2. Preparation of Selenides

3.2.1.1. Electrophilic Selenenylation of Carbonyl Compounds

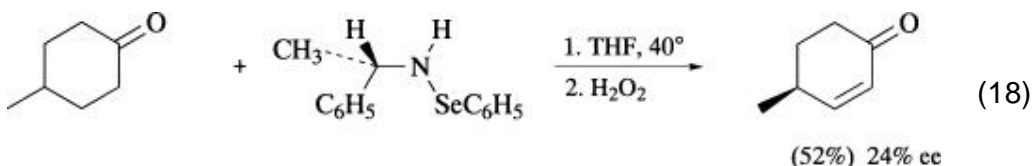
A number of options are available for the conversion of a carbonyl compound to an α -phenylseleno carbonyl compound by electrophilic selenenylation.

3.2.1.1.1. Selenenylation of Enols

The simplest procedure is the direct reaction of a carbonyl compound with a suitable selenenylating agent. Such reactions occur through enols, and are analogous to α -halogenations. Easily enolizable ketones and aldehydes are selenenylated by treatment with benzeneselenenyl chloride, usually with acid catalysis. (3) Benzeneselenenyl bromide usually gives α bromination as the principal reaction, (2) but successful selenenylations have been reported. (96)

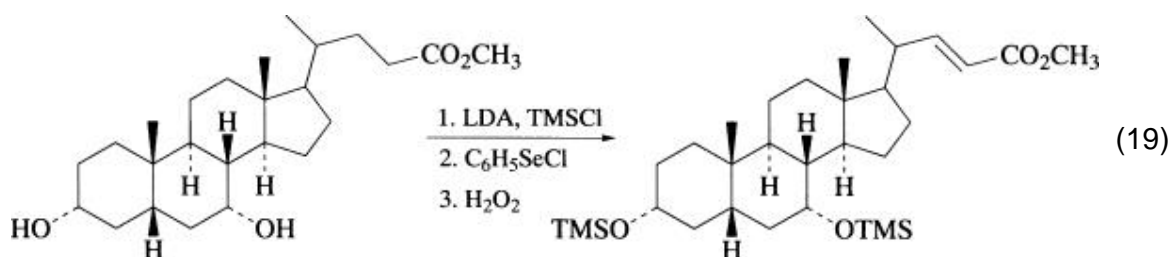
Related procedures under weakly basic conditions involve the treatment of β -dicarbonyl compounds with selenenyl chloride-pyridine (97) or with selenenamides, (64) and aldehydes with selenenamides. (65) Because the enolization is under thermodynamic control, clean monoselenenylation is not always possible with these procedures. The method does not work with esters, amides, lactones, acids, and nitriles because the concentration of the enol form is too low or the enolization process too slow. Selenenylation seems to be more susceptible to steric effects than the bromination of ketones. (98) Some

asymmetric induction is achieved when selenenylation of 4-alkylcyclohexanones is carried out with a chiral selenenamide formed from α -methylbenzylamine (Eq. 18). (99)



3.2.1.1.2. Selenenylation of Enol Silyl Ethers

The selenenylation of enol silyl ethers is the method of choice in any situation where the silyl ether is readily available. Enol silyl ethers react with benzeneselenenyl chloride or bromide quantitatively and rapidly even at -78° . (100) The extra step of forming the enol silyl ether (compared to direct selenenylation of the lithium enolate, see next section) is often justified since higher yields and cleaner products are obtained. (47, 101-105) The common problem of contamination with starting ketone, which can occur both during selenenylation of enolates or enol silyl ethers, can be minimized by using an in situ selenenylation procedure (enolization with amide base in the presence of trimethylsilyl chloride). (106, 107) A further simplification can sometimes be achieved by addition of the selenenyl chloride directly to the enolization–silylation reaction mixture. In this way, methyl chenodesoxycholate is converted to the silylated dehydro compound in good yield, with the crude α , β -unsaturated ester contaminated by only 1.3% of starting material (Eq. 19). (35)



3.2.1.1.3. Selenenylation of Metal Enolates

This is the most commonly used procedure for α selenenylation. A carbonyl compound is treated with lithium diisopropylamide or another suitable strong base (usually at low temperature in tetrahydrofuran). The enolate solution is then allowed to react with one of several selenenylation reagents. The most general reagents are benzeneselenenyl chloride and bromide, which work well

with almost all types of enolates. Diphenyl diselenide is much less reactive and wastes one of the selenium groups, but gives good results with ester, amide, and carboxylate enolates (there is one report of a successful reaction with a ketone enolate, (108) and an unsuccessful one with a lactone enolate (58)).

The most common side reaction (assuming enolate formation is uneventful) is proton transfer during the selenenylation, leading to bis selenenylation and/or recovery of unreacted starting material. Selenium acidifies α -protons [e.g., the pK_a (dimethyl sulfoxide) of acetophenone is 24.7, that of α -phenylselenoacetophenone is 18.6 (109)] and thus proton transfer between starting enolate and product is thermodynamically favored. This side reaction is especially severe when the selenenylation site is unhindered, and proton transfer is consequently relatively rapid (e.g., unbranched nitriles (38)). Proper choice of reaction conditions can improve the situation (low temperature, rapid addition of the selenenyl halide to the enolate, use of two equivalents of base, and/or inverse addition) but proton transfer cannot always be avoided completely.

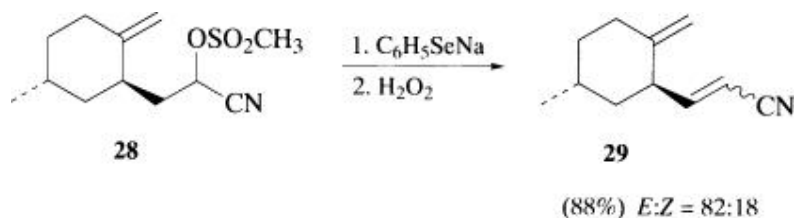
There are numerous cases of successful enolate selenenylations in the presence of functional groups with acidic protons such as secondary amides, (110) secondary sulfonamides, (111) amines, (112) and alcohols. (113-120)

3.2.1.2. Nucleophilic Selenium Reagents

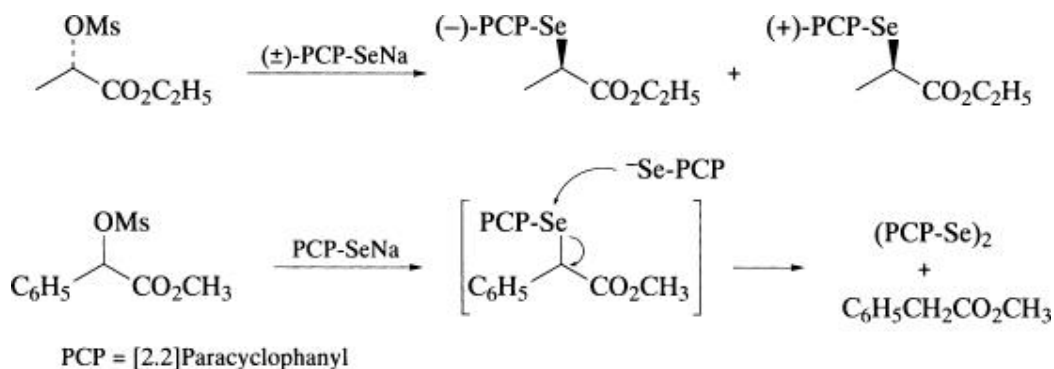
Three principal procedures have been developed for the preparation of α -phenylseleno carbonyl compounds using donor organoselenium reagents: the nucleophilic substitution of α -halo carbonyl compounds with selenolates, the alkylation of selenide enolates, and the acylation of α -lithio selenides.

3.2.1.2.1. Nucleophilic Substitution of α -Halo or α -Sulfonyloxy Carbonyl Compounds

This is the preferred procedure for the large-scale preparation of simple selenides such as phenylselenoacetic acid, (121) ethyl phenylselenoacetate, ethyl phenylseleno-propionate, (54, 122) phenylselenoacetophenone, (123) phenylselenoacetone, (75) and phenylselenoacetonitrile. (57) This method complements enolate selenenylation, since it is just for these simple substrates that polyselenenylation is the most serious problem. Occasionally more complex selenides are prepared in this way. Treatment of mesylate 28 with base does not form useful amounts of 29, but the substitution–oxidation sequence works well. (124)



Application of the substitution reaction is limited by the easy reduction (deselenation) of the selenides or halide precursors by selenolate ion. Thus the mesylate of ethyl lactate reacts smoothly with sodium benzeneselenolate to give the expected selenide. However, a similar reaction with methyl mandelate fails, and only methyl phenylacetate is isolated. (125) To avoid reduction, mesylates, tosylates, and chlorides are preferred; bromides may work; iodides are usually not satisfactory substrates. (123)

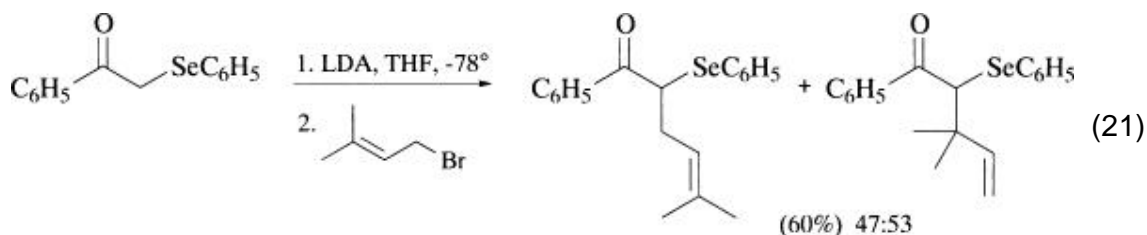
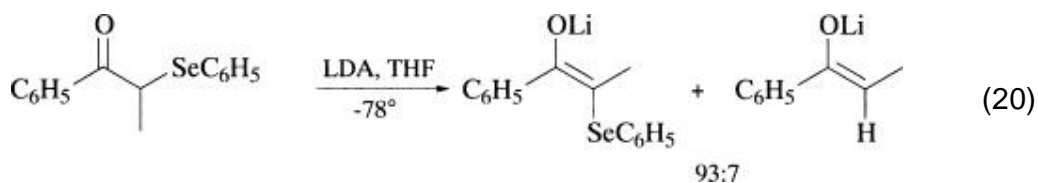


3.2.1.2.2. Alkylation of α -Phenylseleno Carbonyl Compounds

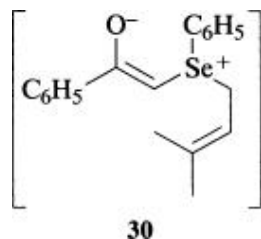
A number of successful alkylations and aldol reactions with metalated α -seleno ketones, esters, lactones, carboxylic acids, and nitriles have been reported. The acidifying effect of a phenylseleno group is only slightly lower than that of a phenylthio group, (109) and the derived enolates behave similarly.

In addition to the normal limitations on $\text{S}_{\text{N}}2$ alkylations of enolates, some side reactions peculiar to selenides have been identified. α -Selenocarbonyl compounds are subject to nucleophilic attack on selenium, the facility of this reaction depending primarily on the stability of the enolate leaving group and the nature of the nucleophile. Thus alkyllithium reagents can rarely be used to deprotonate selenides, and even relatively non-nucleophilic nitrogen bases such as lithium diisopropylamide can cause deselenation to varying degrees

(Eq. 20). (126) Alkylation of some α -phenylseleno enolates gives substantial amounts of products from the rarely seen S_N2' reaction (Eq. 21). This reaction may proceed by alkylation on selenium to



form an intermediate ylid **30**, (126) although another explanation has been proposed. (127) The extent of this reaction varies from as much as 50% for the alkylation of phenacyl phenyl selenide to <1% for ethyl phenylselenoacetate.

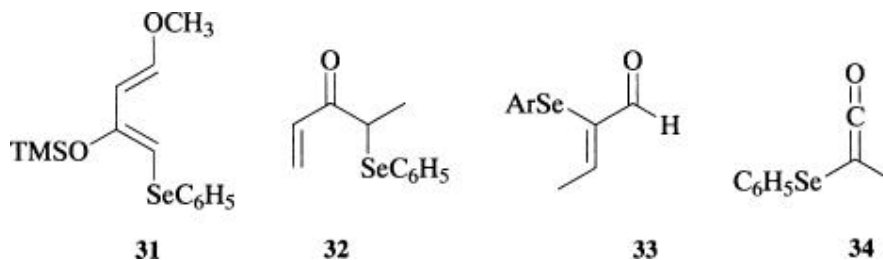


3.2.1.2.3. Acylation of α -Lithio Selenides and Selenoxides

These procedures are used rarely, and so are not discussed in detail here. (16, 17, 128-130)

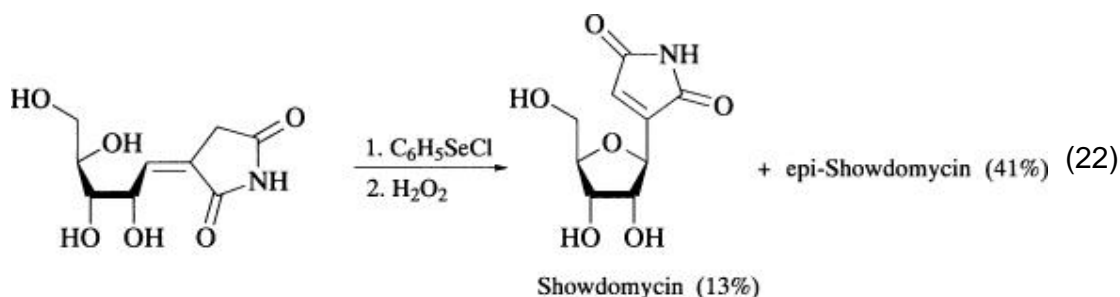
3.2.1.3. Cycloaddition Reactions of Selenides

α -Phenylseleno carbonyl compounds are also prepared by cycloaddition reactions of suitable selenium substituted substrates. Phenylseleno substituted dienes **31** (131) and dienophiles **32**, (132) **33** (133) can be used in Diels-Alder cycloadditions; ketenes bearing phenylseleno groups are used for [2 + 2] cycloadditions **34** (54, 55)



3.2.1.4. Miscellaneous Methods for the Preparation of Selenides

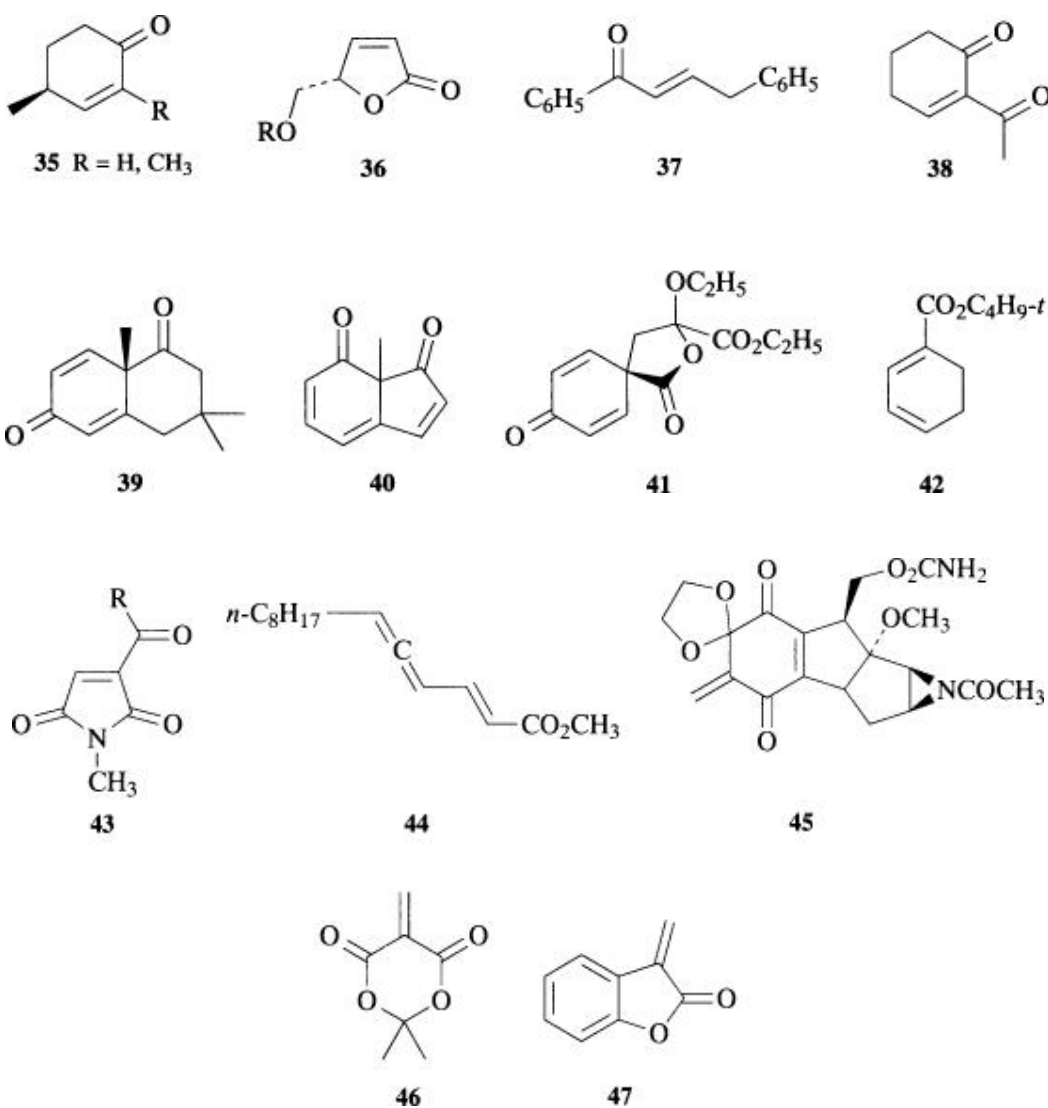
In addition to the procedures described above, there are numerous others which have been used for the preparation of selenides. Such methods include the hydrolysis of α -phenylseleno hydrazones; (134) the oxidation of β -hydroxy selenides; (135-140) the oxidative selenylation of olefins; (137, 141-144) the addition of selenenic acid derivatives to α , β -unsaturated carbonyl compounds; (41, 145-147) the addition of selenenic acid derivatives to acetylenes; (63a-148) the reaction of alkynyl boranes with selenenyl halides; (149) the reaction of diazo compounds with diselenides, selenenyl chlorides, and selenols; (150-155) the reaction of diazo compounds with selenoesters; (156, 157) and Pummerer reactions of keto selenoxides. (158) Table I summarizes the available procedures. None of these methods has been used widely enough to warrant detailed discussion. They do, however, allow the synthesis of a variety of unusual compounds. For example, the preparation of showdomycin and its epimer was achieved by seleno-etherification of an unsaturated cyclic imide (Eq. 22). (145)



Selenides are not commonly carried through many steps in a synthesis because they react with oxidizing agents and nucleophiles. However, it is possible to oxidize alcohols to ketones with manganese dioxide or other oxidants in the presence of the selenide group. (136, 159, 160) Ketals, (160a-161) imides, (162) esters, (163) and enamines (164) can be hydrolyzed; lactones and esters can be reduced, (165, 166) and carboxylic acids can be esterified. (148)

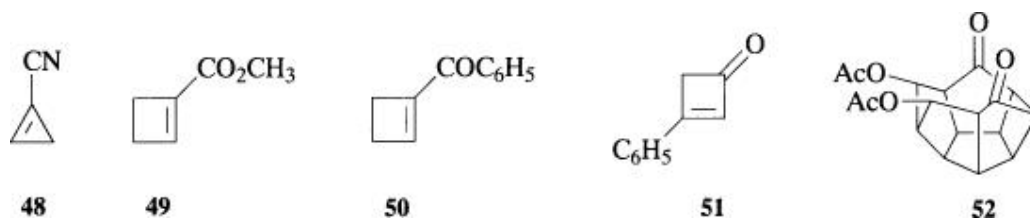
3.3. Preparation of α -Seleninylated Carbonyl Compounds and Elimination to Form Olefins

A principal advantage of the selenoxide *syn* elimination over all other procedures for the preparation of α, β -unsaturated carbonyl compounds is the mildness of the olefin forming step. This has permitted the preparation of a number of very sensitive compounds for which other methods have failed, or are likely to fail. Some compounds in this category are enones with easily enolizable protons: **35**, (167) **36**, 168, 168a **37**, (1) and **38** (2); cyclohexadienones and dihydroaromatic compounds: **39**, (169) **40**, (170) **41**, (171) and **42**; (111) very reactive Michael acceptors: **43**, (172-174) **44**, (175) **45**, (96) **46**, (176) and **47**. (177)

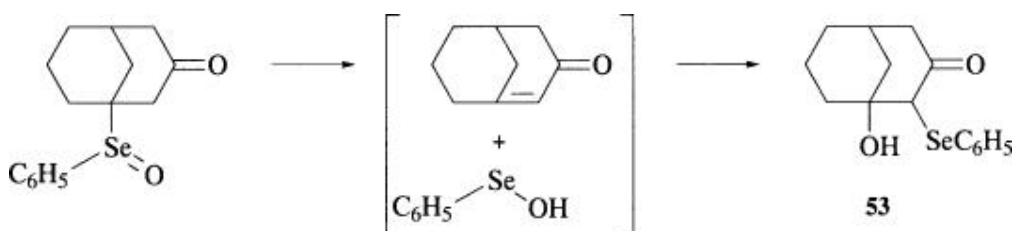


The selenoxide elimination has been used to prepare strained olefins. Examples of cyclopropenes (**48**, captured as a Diels-Alder adduct (**57**)),

cyclobutenes (49, (178) 50, 51 (2)) and bridgehead olefins in the peristylane–dodecahedrane area, captured in situ with acetic acid to give 52, (179) have been reported. An attempted synthesis of



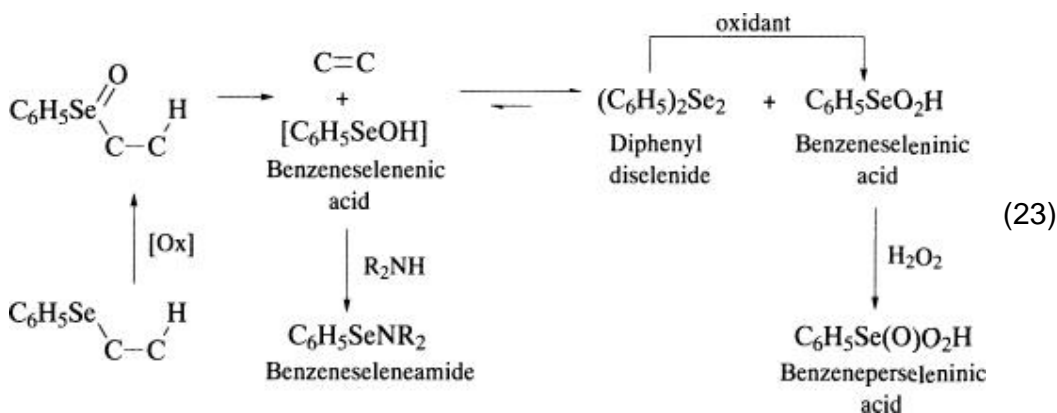
1-benzoylcyclopropene was unsuccessful. (2) Bicyclo[3.3.1]non-1-en-3-one was apparently formed by a selenoxide elimination (the selenium was β to the ketone), but the intermediate bridgehead enone was trapped by selenenic acid to give the α -phenylseleno- β -hydroxy ketone 53. (180)



3.3.1.1. Oxidation of Selenides

Equation 23 shows the relationship between the various selenium species that are formed during the oxidation of a selenide and the *syn* elimination of selenoxides.

The conversion of an α -phenylselenocarbonyl compound to the corresponding olefin by oxidation and selenoxide elimination can be carried out under a variety of

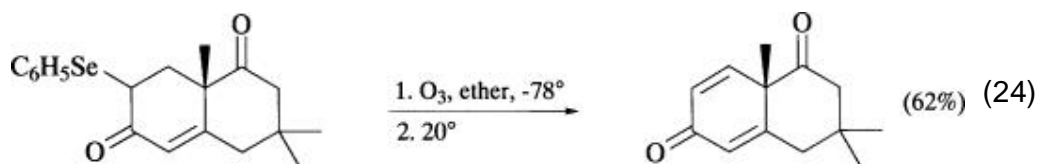


The simplest and most frequently used procedure for selenide oxidation and elimination is to treat the selenide with 15–30% aqueous hydrogen peroxide at 0° to room temperature. Solvents like dichloromethane (with or without an equivalent of pyridine) or tetrahydrofuran (with a trace of acetic acid) are most frequently used. The stoichiometric reaction requires two equivalents of hydrogen peroxide, although an excess is usually used to ensure complete oxidation of all selenium materials to the Se(IV) oxidation state (C₆H₅SeO₂H is the product formed). In some cases excess hydrogen peroxide may be required because selenium intermediates can catalytically destroy some of the peroxide. (27) The actual oxidant is probably benzeneperseleninic acid (C₆H₅Se(O)OOH), formed by reaction of benzeneseleninic acid with hydrogen peroxide. (194-197) For this reason functional groups that are normally stable to hydrogen peroxide may be co-oxidized when seleninic acids are present.

Overoxidation to form Se(VI) compounds (selenones and selenonic acids) is not a problem. There are, however, several examples where excess hydrogen peroxide oxidizes the product. For these a stoichiometric amount of peroxide may work, or one of the alternative oxidants described below may be used. Thus to achieve useful yields of β-dicarbonyl enones it is necessary to use the exact stoichiometric amount of oxidant (2 equivalents). (2) Cyclobutanones (2) and strained cyclopentanones are subject to Baeyer–Villiger oxidation. (198) Oxidation of several 16-phenylseleno-17-ketosteroids with hydrogen peroxide produces δ-lactones as the only identified products (see Eq. 45). (199, 200)

3.3.1.1.3. Ozone

Selenides are quantitatively and cleanly oxidized to selenoxides with ozone at –78°. Selenones are not formed in significant amounts. Since there are no byproducts, ozone is the best reagent for forming selenoxides when special conditions are required for the thermolysis step, or where simplicity of workup is crucial. An example is the formation of the extremely acid and base sensitive 4-acylcyclo-hexadienones (Eq. 24). (169) Oxidation of the selenide with hydrogen peroxide gives quantitative aromatization. *m*-Chloroperoxybenzoic acid gives the desired dienone, but it cannot be purified. However, low temperature ozonation followed by warming gives a good yield of dienone.



3.3.1.1.4. *m*-Chloroperoxybenzoic Acid (MCPBA) and Other Peracids

m-Chloroperoxy-benzoic acid in dichloromethane or tetrahydrofuran will oxidize most selenides below their decomposition temperature (-50° to -78°), and can thus also be used for those situations where the product olefin may be sensitive to the oxidant, or where special reaction conditions are required for the thermolysis. The presence of acid during selenoxide eliminations is undesirable (see below). For this reason, the reaction mixture is normally buffered with a secondary or tertiary amine before the temperature is raised to initiate fragmentation.

A combination of *m*-chloroperoxybenzoic acid and hydrogen peroxide has been used to oxidize selenides. (201-203) The role of the hydrogen peroxide is presumably to oxidize selenenic acid and diphenyl diselenide, which are formed during the elimination, to seleninic acid.

3.3.1.1.5. Sodium Metaperiodate

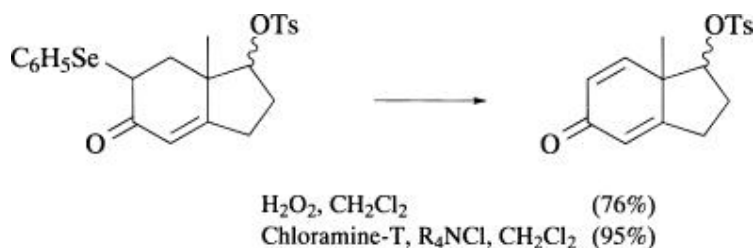
Sodium metaperiodate is insoluble in organic solvents, and so it must be used in aqueous methanol, tetrahydrofuran, ethyl acetate, or glyme. 18-Crown-6 can be added to help solubilize it. (204) Periodate has been frequently used to oxidize selenides when the product or starting material contains other oxidizable functions. It appears to be the oxidant of choice for aldehydes, and has been successfully used to oxidize selenides which contain amine functions. (187, 189, 205, 206) Electron-rich double bonds (e.g., trialkyl substituted) can be epoxidized by hydrogen peroxide when seleninic acid is present. (196, 195) Periodate is frequently used in such situations. (3, 58, 207-209)

3.3.1.1.6. Oxaziridines

Superior yields of several enones by oxidation with 2-*p*-toluenesulfonyl-3-phenyloxaziridine have been reported. (210-213)

3.3.1.1.7. Chloramine-T (TsNCINa)

Alkyl selenides sometimes give superior yields of olefins when treated with anhydrous Chloramine-T instead of with an oxygen-based oxidant. A similar observation has been made for an α -phenylseleno ketone. (214)



3.3.1.1.8. Other Oxidants

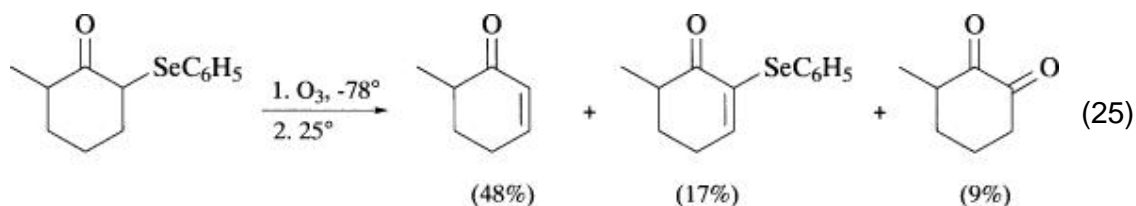
Other oxidants that have been used successfully are *tert*-butyl hydroperoxide, (47) bromine/bis(tributyltin)oxide, (57) *N*-chlorosuccinimide/water, (57, 215) *tert*-butyl hypochlorite/methanol/sodium bicarbonate, (47, 215) *N*-bromosuccinimide/sodium acetate, (39) singlet oxygen, (34) chromium trioxide-pyridine, (216) and sulfuryl chloride/sodium bicarbonate. (72)

3.3.1.1.9. Side Reactions during Selenoxide Eliminations

There are a number of selenides for which the simple oxidation with excess hydrogen peroxide or other oxidants gives unsatisfactory yields of α , β -unsaturated carbonyl compounds. Unfortunately, in only a very few cases was the reason for the failure elucidated and reported (e.g., by identification of the products formed). Thus it is frequently not known whether the selenenylation, the oxidation, or the elimination went awry. The systems which have been most problematic are those in which the double bond being formed is strained or where the C - Se bond and C - H bonds which are breaking during the selenoxide elimination are poorly aligned, as in some cyclic systems.

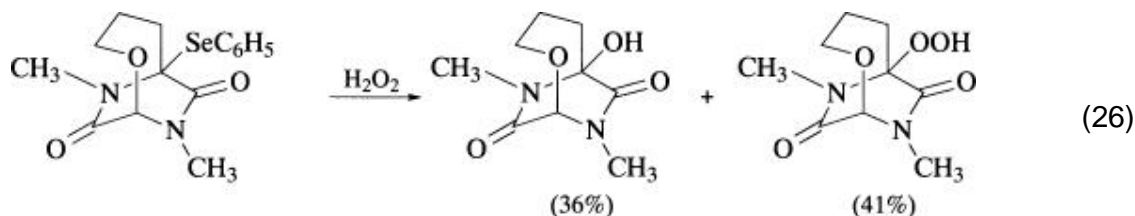
Selenoxides are reactive compounds. In addition to the desired *syn* elimination, a number of other reactions may occur, depending on the structure of the selenoxide and the reaction conditions. The side reactions that have been identified are the following:

1. Seleno-Pummerer reaction of secondary selenoxides. This reaction forms α -dicarbonyl compounds and their oxidation products (Eq. 25), (2, 217) and can be effectively prevented by carrying out the selenoxide elimination under weakly basic conditions. See the section on Ketones for a more detailed discussion.

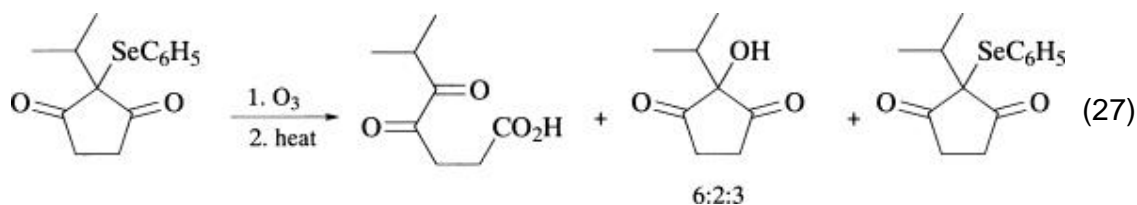


2. Reaction of selenenic acids (which are the initially formed selenium products in the selenoxide elimination) with nucleophilic sites in the molecule. Selenenic acids will react with nucleophilic olefins such as enols, enol ethers, and enamines as well as with ordinary alkenes, but not usually with electron-deficient olefins. (2, 27) When activated aromatic rings (phenols) are formed, such side reactions can be effectively prevented by introducing a selenenic acid scavenger (e.g., 3,5-dimethoxyaniline (213, 218)). Selenenic acid can also cause α -selenenylation of the intermediate selenoxide (which may be readily enolizable if the selenoxide is secondary), resulting in the formation of vinyl selenide products. This reaction may not be recognized when excess hydrogen peroxide is used as oxidant since further oxidation of the vinyl selenide will occur. See the section on Ketones for a more detailed discussion.

- Baeyer–Villiger oxidation of starting selenide, intermediate selenoxide, or product by hydrogen peroxide–benzeneseleninic acid (see Ketones, below).
- Carbonium ion reactions of the selenoxide. Selenoxides are protonated under relatively weakly acidic conditions; they are more basic than sulfoxides by ~4 pK_a units (pK_a of thiolane oxide: -1.34, (219) pK_a of 3,3-dimethylselenolane oxide: 3.06 (28). Thus, if there are carbonium ion stabilizing groups such as nitrogen or oxygen at the α carbon, and if the selenoxide elimination is difficult, ionic processes can predominate. Equation 26 may be an example of this effect. (60)

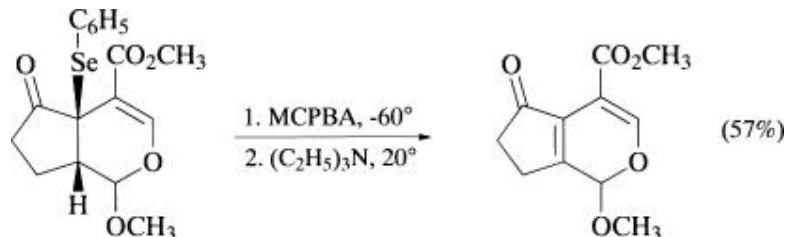


- Free radical decomposition of the selenoxide. The products obtained in Eq. 27 have been ascribed to homolytic decomposition of the selenoxide. In this case sulfoxide elimination is more successful. (220, 221)

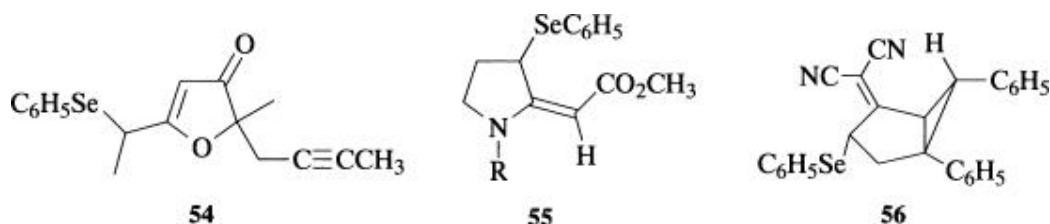


- Reduction of intermediate selenoxide back to starting material. The benzeneselenenic acid formed during the selenoxide elimination is a weak reducing agent under acidic conditions. Thus, if the use of excess oxidant is not feasible and the reaction mixture is acidic during the selenoxide elimination, considerable selenide may be recovered even if oxidation to selenoxide was complete (Eq. 27).
- Nucleophilic addition to the product olefin. If the product is a strained olefin, it may react with adventitious nucleophilic species; sometimes conditions are deliberately arranged to capture such olefins in this way before they decompose. (179, 221)
- [2.3]-Sigmatropic rearrangements of allylic, allenic, or propargylic selenoxides to give allylic alcohols. The *syn* elimination and [2,3]-sigmatropic rearrangements are energetically closely balanced, but the latter will normally be the faster process. (222, 223) However, when the double bond must be moved into a thermodynamically less stable position during the rearrangement, the *syn* elimination can be a competing or principal reaction. (224) This is probably the reason for the successful selenoxide

eliminations of Eq. 5 (40) and Eq. 28. (225)



γ -Phenylseleno- α , β -unsaturated carbonyl compounds (e.g., **54** (226) and **55** (227)) and nitriles **56** (228), produced by selenenylation of dienolates, usually give elimination rather than rearrangement products on oxidation (Eq. 5), (40) although there are exceptions. (229) Allylic alcohols are reported as byproducts in the seleninylation of lactones with benzeneseleninic anhydride. (86)



3.3.1.1.10. Avoiding Side Reactions during the Selenoxide syn Elimination

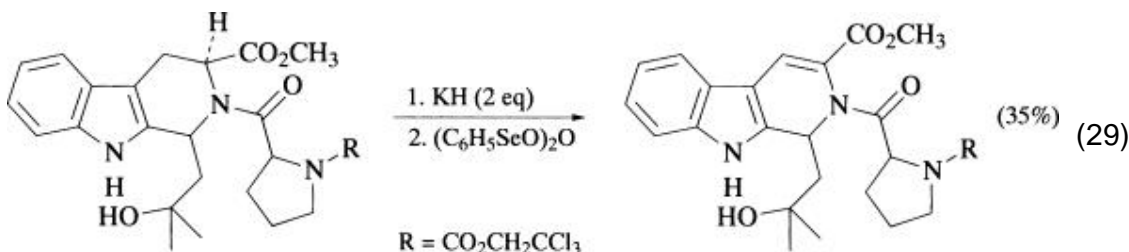
A simple procedure will prevent or reduce those side reactions above which are acid catalyzed (items 1, 4, and 6) and which involve selenenic acids (items 2 and 6): the oxidation should be carried out at low temperature with *m*-chloroperoxybenzoic acid or ozone, and a solution of the selenoxide should then be treated with an amine and briefly thermolyzed in refluxing methylene chloride or carbon tetrachloride. (2, 47) The choice of amine is dictated by the reactivity of the olefin being formed: an unhindered secondary amine is best, but even a hindered tertiary amine will help. If an amine cannot be used, a nucleophilic olefin such as a vinyl ether should be substituted. (179) It is also important to use the least polar solvent possible especially when carbonium ion side reactions (item 4) are a possibility.

3.3.1.2. Direct Introduction of Seleninyl Groups

An alternative to introducing a phenylseleno group and then oxidizing it is to introduce a selenoxide function directly. Although this would seem to be an attractive solution, it has not been used as widely as the two-step process.

3.3.1.2.1. Seleninylation of Enolates

The reaction of enolates with benzeneseleninyl chloride (2) or benzeneseleninic anhydride (230) has been used infrequently (only 5 examples were found). In one of these, standard selenenylation–oxidation failed, but reaction of the potassium enolate with benzeneseleninic anhydride gave the desired product (Eq. 29). (230) In a second example, the direct seleninylation was needed to avoid oxidation of a sulfide group present in the molecule (Eq. 17). (84)

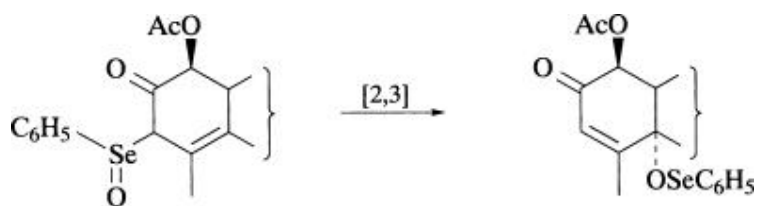
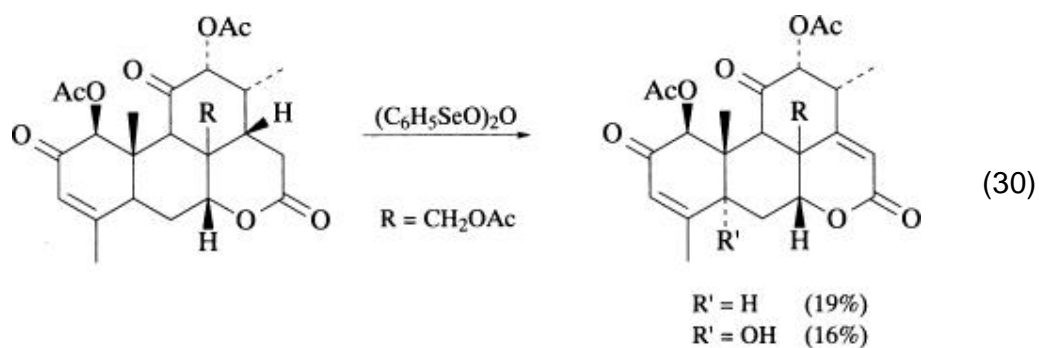


3.3.1.2.2. Seleninylation of Enols

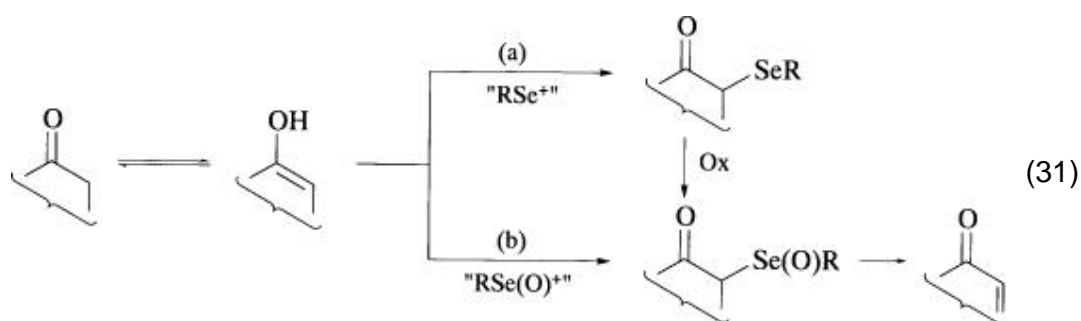
Several classes of carbonyl compounds can be dehydrogenated by treatment with benzeneseleninic anhydride at elevated temperatures (typically 80–120°, although lower temperatures can be used in the presence of acid catalysts (231)). Although this method involves much more vigorous reaction conditions than the two-step process, it has the advantage of convenience and easy scale-up. The reaction depends on the capture of enolic intermediates by electrophilic selenium species, so it is limited to easily enolizable carbonyl compounds. α , β -Unsaturated ketones, (14, 89, 92) δ -lactones, (86, 88, 232, 233) 4,5-dihydro-1,3-oxazoles, (90) and δ -lactams (91) have been prepared in this way.

Several reagents have been used and benzeneseleninic anhydride is the most common. Benzeneseleninic acid also works, presumably by dehydrating to the anhydride under the reaction conditions. (90) A catalytic amount of benzeneseleninic anhydride or diphenyl diselenide in the presence of an oxidant such as *tert*-butyl hydroperoxide, (14) iodoxybenzene, or *m*-iodoxybenzoic acid (89, 92) is also effective, less expensive, and simplifies purification of the product.

γ -Hydroxylation products are sometimes seen during benzeneseleninic acid oxidations. These probably arise by [2,3]-sigmatropic rearrangement of allylic selenoxide intermediates (Eq. 30). (86, 233)



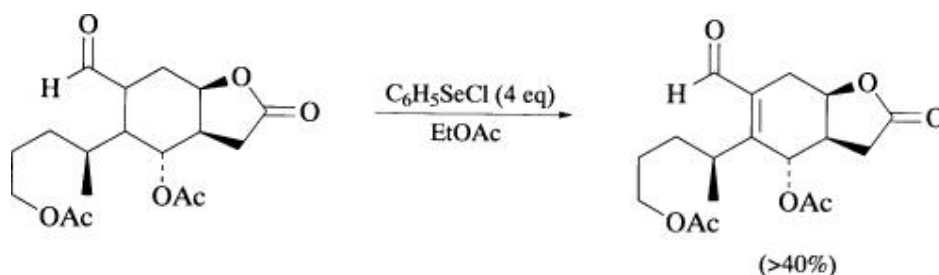
The mechanistic path for the reaction of carbonyl compounds with benzeneseleninic anhydride or diphenyl diselenide/iodoxybenzene is not well established. Two alternatives are the selenenylation of the enol (Eq. 31, path a), followed by oxidation of the selenide by one of the available oxidants, or the seleninylation of the enol (path b). Both selenenylating [ArSeOH, ArSeOSe(O)Ar] and seleninylation (ArSeO₂H, [ArSeO]₂O) species are undoubtedly present. The former species are more reactive toward enols, but the latter probably exist in higher concentration. Therefore, an a priori decision as to which pathway is followed cannot be made, and no experimental tests have been reported.



3.4. Preparation of α , β -Unsaturated Aldehydes

3.4.1.1. Selenides

Since aldehyde metal enolates are not routinely available by the usual lithium amide metalation procedure, the majority of α -phenylseleno aldehydes have been prepared by selenenylation of aldehyde enols, enol ethers, or enamines. The reaction of aldehydes directly with benzeneselenenyl chloride (3) or 2-pyridineselenenyl bromide (47, 234) can be used for simple systems. In a few cases, the α, β -unsaturated aldehydes can be formed directly on treatment with excess benzeneselenenyl chloride. (97, 235) The mechanism of this direct reaction is not known, but probably involves excess selenenyl chloride as the oxidizing agent.



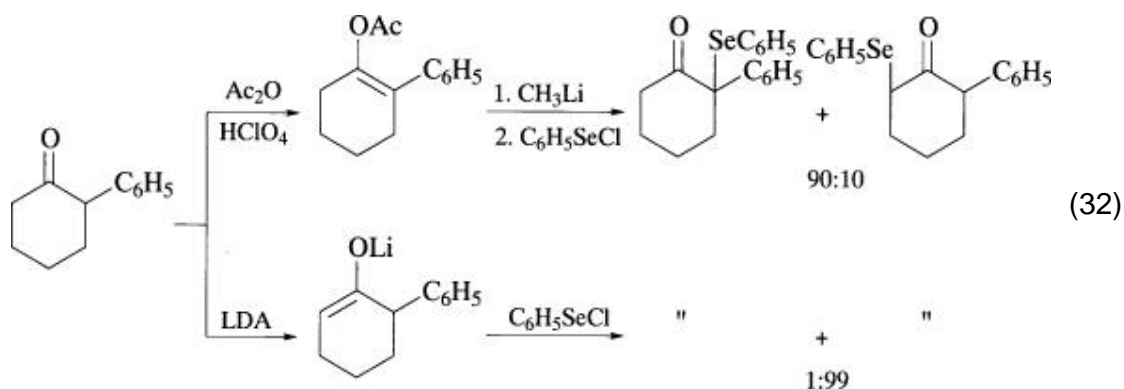
Aldehydes can also be selenenylated by treatment with *N,N*-dialkylbenzeneselenenamides. (65) This reaction may involve selenenylation of the enol or enolate by the protonated selenenamide, or it may proceed through an intermediate enamine. It is not necessary to isolate the selenenamide, it can be prepared in situ by the reaction of, for example, two equivalents of morpholine with benzeneselenenyl bromide. (80) Both mono- and diselenenylated products can be obtained. A number of aldehydes have also been selenenylated through their enamines. (164) The selenenylation step must be carried out at low temperature to avoid deleterious side reactions.

3.4.1.2. Oxidation

Hydrogen peroxide is occasionally used for the oxidation of α -phenylseleno aldehydes, but can lead to overoxidation and the formation of α, β -unsaturated carboxylic acids. (236, 237) Thus milder and easily controllable reagents such as sodium metaperiodate, *m*-chloroperoxybenzoic acid, and ozone are more commonly used.

3.5. Preparation of α, β -Unsaturated Ketones

The selenenylation of unsymmetrical ketones is complicated by considerations of regiochemistry. Fortunately, effective strategies are available for enol, enol ether, and enolate regiocontrol. Kinetic control is typically obtained through the enolate, and thermodynamic control via the enol, enol silyl ether, or enol acetate (Eq. 32). (217)

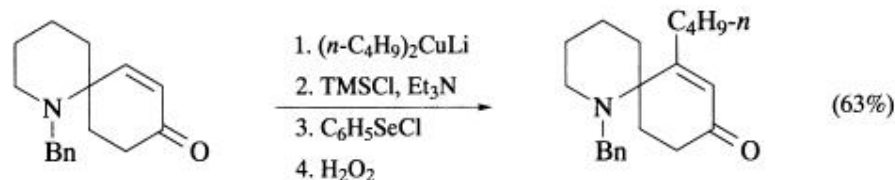
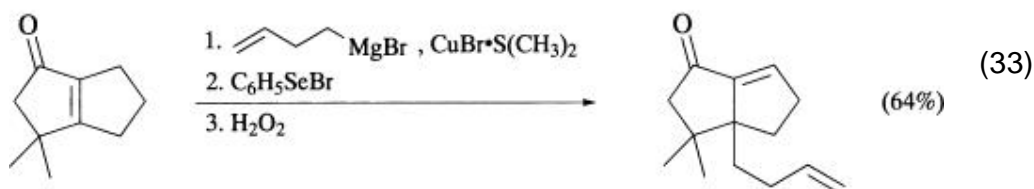
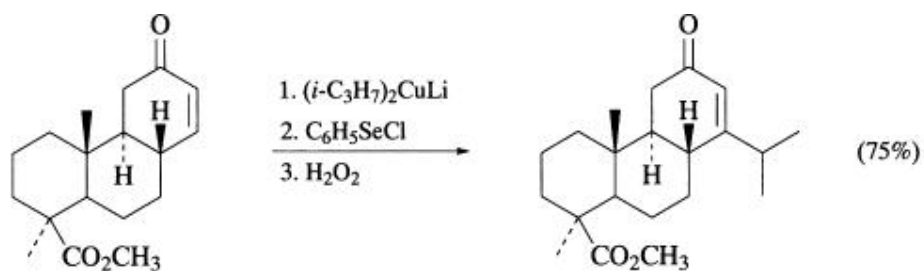


Both enol silyl ethers and enol acetates can be cleaved to form enolates with methyl lithium, (2, 238) or they can be selenenylated directly. (2, 4) Other procedures produce a regioselective enolate as an initial product of another reaction, such as conjugate addition to or conjugate reduction of an α, β -unsaturated ketone, reaction of diazoketones with organoboranes, (239) and the anionic oxy-Cope rearrangement. (240) These enolates can then be selenenylated directly, or trapped as enol ethers and subsequently converted to selenides.

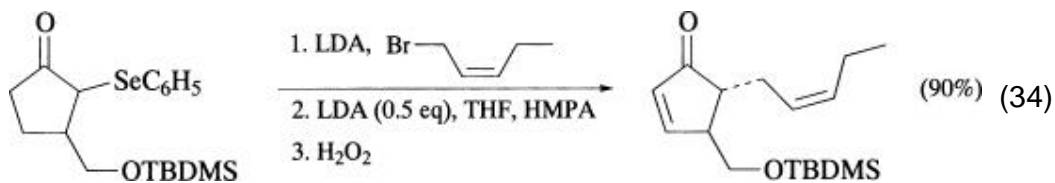
3.5.1.1. Selenenylation of Enolates

The most common procedure for the introduction of selenium α to keto groups is the reaction of enolates with benzeneselenenyl chloride or bromide. The selenenylation is fast, and usually no regioisomeric equilibration of enolates occurs during the selenenylation if the reaction is carried out under mild conditions. The enolates are normally prepared by lithium amide deprotonation of the ketone, but occasionally triphenylmethyl lithium is used to achieve higher regioselectivity. (241)

Conjugate addition of organocuprates, (52, 64, 211, 212, 242, 243) alkylboranes, (239) or nickel reagents (244) to enones followed by selenenylation of the metal enolate formed and oxidation provides a net β -alkylation of an enone. Although numerous reports of successful one-pot procedures have appeared, there can be difficulties associated with the reaction of the selenenylating reagent with organometallic species remaining in solution. (2) Trapping of the enolate with trimethylsilyl chloride may provide cleaner reaction products (Eq. 33). (245)



Tertiary α -phenylselenoketones can be equilibrated by treatment with lithium diisopropylamide. (246-248) The driving force for the reaction is the formation of the more stable selenium-substituted enolate. The reaction can be used to control α - vs. α' -substitution (Eq. 34). (249)

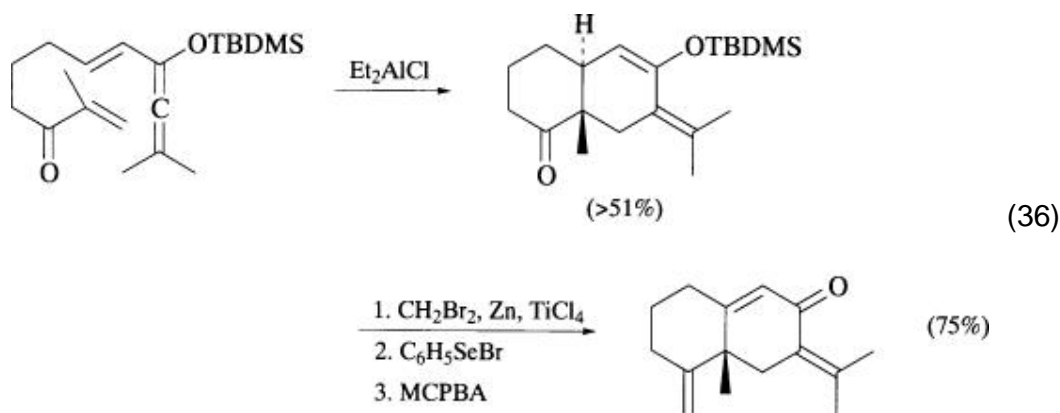
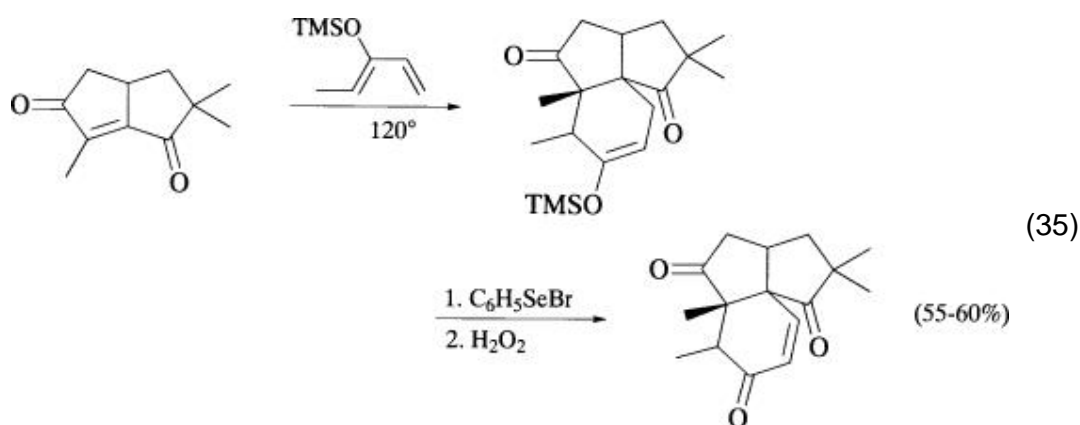


3.5.1.2. Selenenylation of Enol Silyl Ethers

Higher yields have been reported when enolates are first trapped as enol silyl ethers and then selenenylated, compared to direct selenenylation of the enolate or the ketone, and this procedure has become commonly used. (47, 101-105) Thus conversion of cycloheptanone to α -(2-pyridylseleno)-cycloheptanone proceeds in 79% yield using the enolate, 84% by acid-catalyzed selenenylation of the ketone, and 97% yield from the enol silyl ether. (47) One reason for the better results may be that proton transfers between starting enolate and product selenide are prevented, and

thus the method is particularly valuable when the position to be selenenylated is secondary or primary. In addition to producing cleaner products, enol silyl ethers have also been used because thermodynamic control of ketone enolization (production of the more highly substituted enol) is easily controlled under silylation conditions using in situ generated trimethylsilyl iodide. (49, 250, 251)

Cuprate addition to enones followed by silylation prior to selenenylation avoids problems associated with reaction of the selenenylating reagent with organometallic species. (2, 245) Other procedures for enol silyl ether preparation are conjugate additions of silyl ketene acetals to enones, (252) reactions of ketones with silyl triflates (253) or trimethylsilyl iodide, (254, 255) and cycloaddition reactions of siloxydienes (Eqs. 35 (256) and 36 (257)).

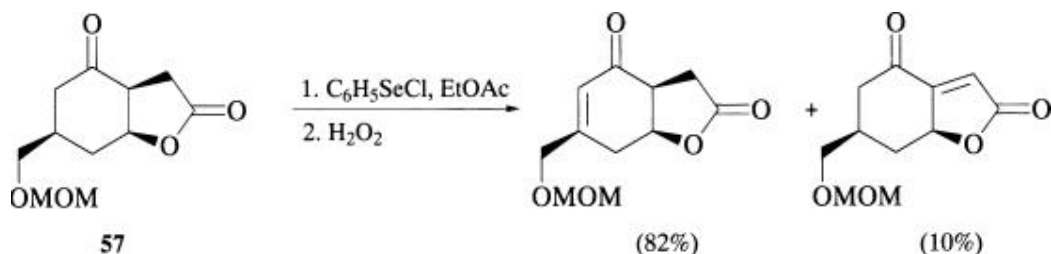
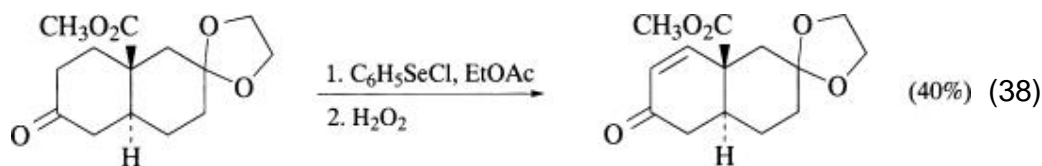
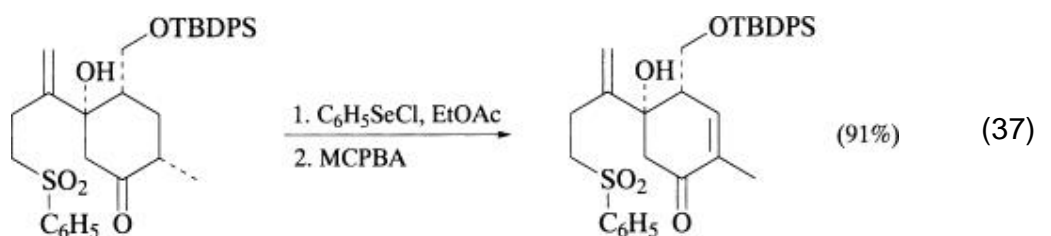


3.5.1.3. Selenenylation of Enols

The simplest procedure for selenenylation of ketones is direct reaction with benzeneselenenyl chloride. Although the reaction conditions are acidic

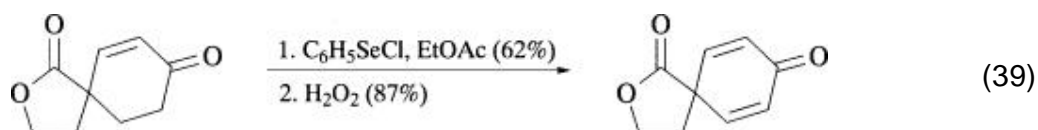
(hydrochloric acid is often added as a catalyst and is in any event formed during the reaction), and the selenenyl chloride is a powerful electrophile, the reaction can be carried out in the presence of a wide range of other functional groups including olefins (simple, (221, 258) enones, (169, 259) and α -methylene lactones (198, 260)), esters, (261) phenols and phenol ethers, (191, 262) amines, (96, 187) ketals, (171, 263-265) tertiary alcohols, (266, 267) protected alcohols, (MOM, (268) TBDMS, (269) and acetate (3, 268)), nitriles, (270) and epoxides. (271) Side reactions that have been identified are multiple selenenylation (272) and the formation of α -chloroselenides. (273) It is possible that the latter reaction is the result of contamination of benzeneselenenyl chloride by phenyl selenium trichloride, which can easily be formed by overchlorination of diphenyl diselenide. (63)

Regioselectivity has not been systematically studied, but appears to be appropriate for an acid-catalyzed enolization process analogous to ketone bromination. In the absence of ring-strain considerations, the more highly substituted position is selenenylated. Thus 2-heptanone gives predominantly hept-3-en 2-one. (3, 261) 2-methylcyclohexanones give predominantly 2-substitution (Eq. 37), (258) *trans*-3-decalones react at the 2 position (steroid numbering, Eq. 38). (264) The bicyclic lactone **57**, however, gives mostly reaction at the less-substituted α carbon. (268)



The reaction of enones with selenenyl halides by using pyridine as catalyst produces α -phenylselenoenones (274) and α -haloenones (275) rather than the α' -phenylselenoenones formed under acidic conditions.

The acid-catalyzed selenenylation is especially useful when base-sensitive functional groups such as electron-deficient double bonds, which might interfere with enolate formation, are present. The penultimate step in the syntheses of aromaticin, (276) ambrosin, (260) and stramonin-B (271) was introduction of a cyclopentenone double bond in the presence of an α -methylene lactone or an α -methylene lactone epoxide. Numerous cyclohexadienones (Eqs. 24 and 39 (259)) can be prepared by dehydrogenation of 4,4-disubstituted cyclohexenones. (169, 171, 277)

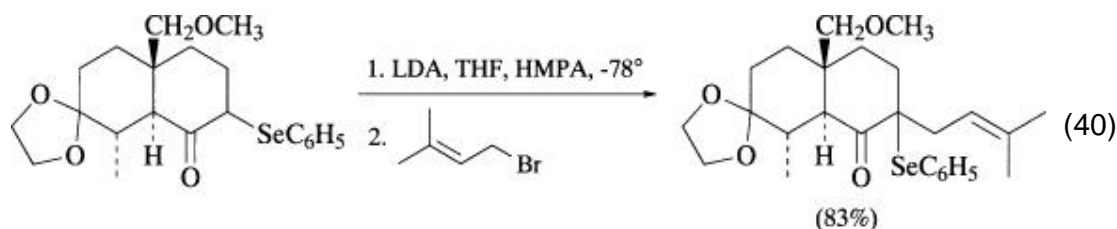


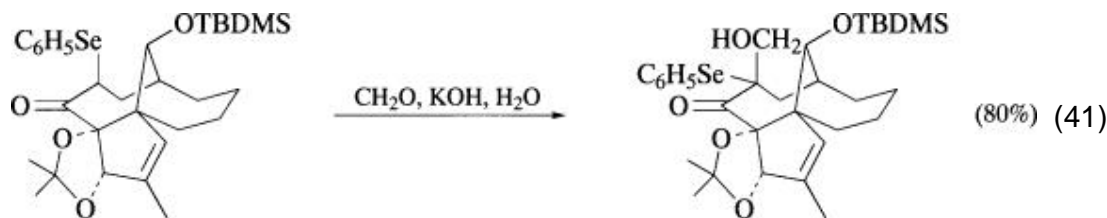
3.5.1.4. Enol Acetates

Most enol acetates do not react with benzeneselenenyl chloride or bromide. It is necessary to either cleave the enol acetate with methyllithium to give an enolate or use a more reactive PhSe^+ source such as $\text{PhSeO}_2\text{CCF}_3$. (2, 4-63a) For this reason enol acetates are infrequently used for the preparation of selenides.

3.5.1.5. Alkylation of Selenium Substituted Enolates

The enolates formed by deprotonation of α -phenylselenoketones (Eq. 20) can be alkylated (Eqs. 34 (249) and 40 (50)) and hydroxyalkylated (Eq. 41) (102).

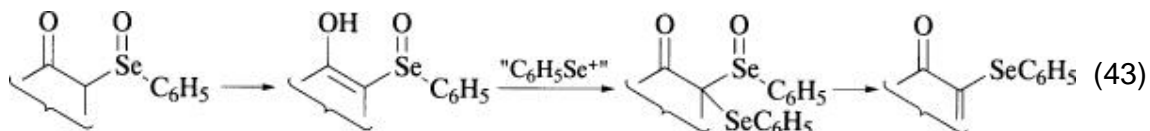
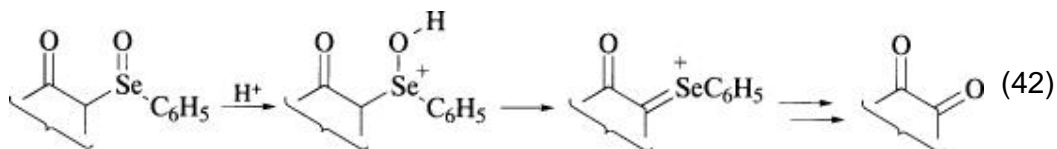




3.5.1.6. Oxidation of α -Phenylseleno Ketones and Formation of Enones

Hydrogen peroxide is the most common reagent for the oxidation of keto-selenides. Keto-selenides are more prone to side reactions during the oxidation–elimination process than are other carbonyl compounds. There are two reasons for this. First, the majority of ketone-to-enone conversions involve secondary selenides, which are especially prone to side reactions. Second, the majority of the examples reported are in cyclic systems (especially cyclohexanones) in which the bond alignment between C - Se and C - H bonds is not optimal. There are thus a number of situations in which the experimentally simple and inexpensive hydrogen peroxide procedure does not give useful yields, and a variety of other oxidants are used.

The most troublesome side reactions are the seleno-Pummerer reaction (Eq. 42) and α -selenenylation of the intermediate selenoxide (Eq. 43). Since both require that



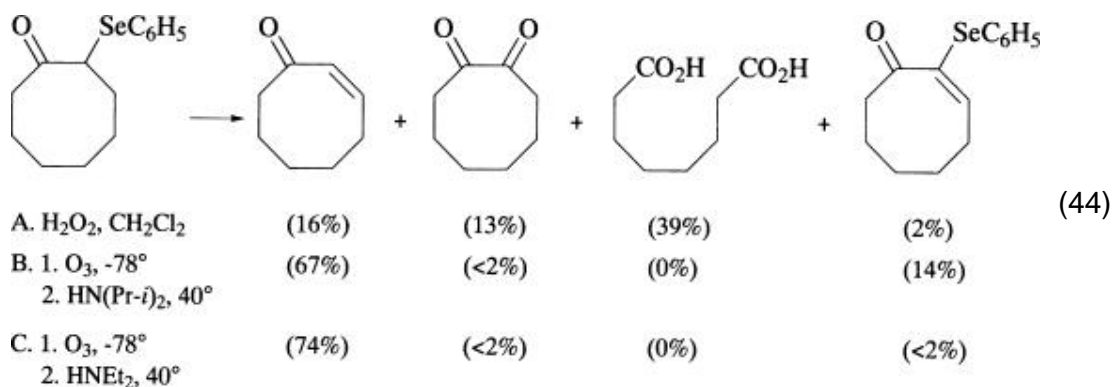
the selenoxide have an α hydrogen, tertiary selenides are in general well behaved. The Pummerer reaction leads eventually to α -dicarbonyl compounds, which may be oxidized further to carboxylic acids by hydrogen peroxide. The intermediate selenonium ion can also be captured by other nucleophiles (e.g., chloride to form an α -chloroenone (199)). The Pummerer reaction requires acid catalysis, and can be effectively prevented by running the reaction under mildly basic conditions. Oxidations with hydrogen peroxide typically occur at temperatures at which the selenoxide elimination is fast and

in addition require weakly acidic conditions. If Pummerer reactions are a problem it thus becomes necessary to separate the oxidation and elimination steps and to use an oxidant other than hydrogen peroxide. Commonly used oxidants are ozone or *m*-chloroperoxybenzoic acid; both react with selenides conveniently in methylene chloride at -78° , conditions under which almost all selenoxides are stable. See the discussion above about oxidants.

The second side reaction (Eq. 43) leads to α -(phenylseleno)enones and products derived from them, (2) and is somewhat more difficult to prevent. Sometimes weak base will be sufficient, but for more difficult cases it may be necessary to specifically trap the benzeneselenenic acid (C_6H_5SeOH) which is the primary product of the selenoxide fragmentation. (278-280) Suitable reagents are unhindered primary or secondary amines, or sacrificial nucleophilic olefins (e.g., 2-methoxypropene). In some cases amines are unsuitable because of their reactivity toward the product enones; in others the selenenamide which is formed during the trapping reaction can react with the enone. (2)

Equation 44 illustrates how the pattern of products varies for oxidation–elimination of α -(phenylseleno)cyclooctanone as a function of reaction conditions. (2)

Run A represents the usual hydrogen peroxide conditions. For Run B, the selenide was first oxidized and the solution was made basic with diisopropylamine before pyrolysis. Note that the Pummerer products (α -diketone and the dicarboxylic acid) are gone, but there is still a considerable amount of selenoenone. In Run C

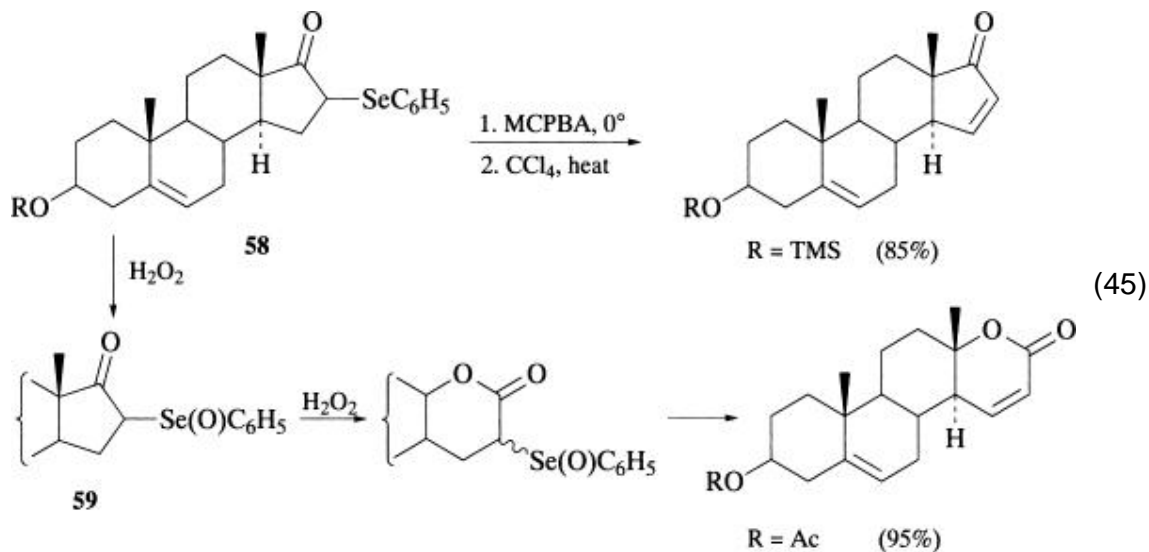


diethylamine was used; this amine effectively traps benzeneselenenic acid ($PhSeOH$) to form *N,N*-diethylbenzeneselenenamide ($PhSeNEt_2$, which can be isolated), and this prevents the second side reaction. (2)

The beneficial effect of conditions such as those in Run C have also been

reported for 2-pyridyl selenides. Although these seem to be a little less prone to side reactions, use of low temperature ozonation followed by pyrolysis in the presence of diethylamine gave the highest yields of a number of oxidation conditions tried. (47)

16-Phenylseleno-17-keto steroids produce a D-ring lactone on oxidation with hydrogen peroxide (Eq. 45). (199, 200) A report to the contrary is probably in error. (281) The

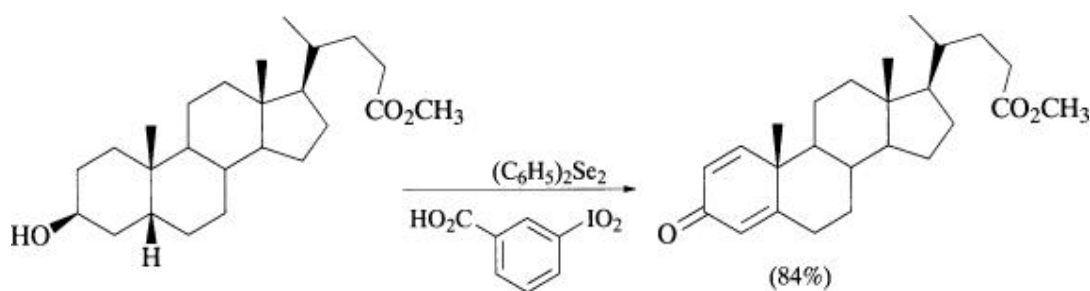


culprit here is the *trans*-D-ring fusion, which makes it energetically unfavorable to introduce planar sp^2 centers. This problem is also encountered, although to a lesser extent, during the preparation of a cyclopentenone *trans*-fused to a seven-membered ring in the ambrosin series. (198) A recent reinvestigation of this question revealed that the oxidation of **58** produces a selenoxide **59** which is stable at room temperature for at least an hour. (35) In the presence of excess hydrogen peroxide, it undergoes Baeyer–Villiger oxidation to the unstable lactone selenoxide, which fragments rapidly. In fact, the Baeyer–Villiger oxidation of **59** is faster than the oxidation of the selenide with hydrogen peroxide, so this side reaction cannot be avoided. Good yields of the desired 15,16-dehydrosteroid are obtained by low temperature oxidation with *m*-chloroperoxybenzoic acid (ozone cannot easily be used here because of the double bond), basic workup at 0° to remove *m*-chlorobenzoic acid (the reaction fails without this step whether or not amine is added), and brief pyrolysis of the selenoxide in refluxing carbon tetrachloride.

3.5.1.7. Preparation of Enones by Dehydrogenation with Benzeneseleninic Anhydride

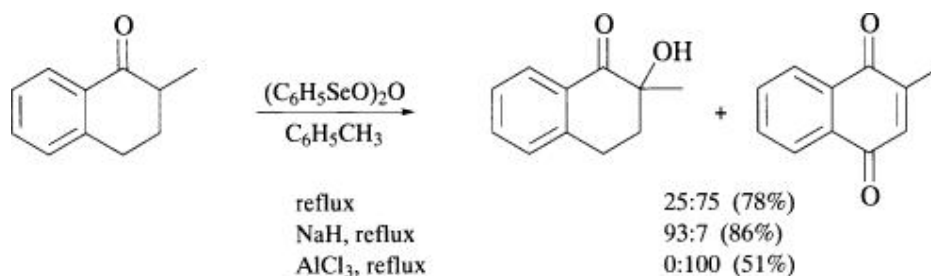
Procedures have been developed for the dehydrogenation of steroidal and other cyclic ketones by heating with benzeneseleninic anhydride.

The reaction presumably involves the seleninylation (or selenenylation) of enols. There is therefore little possibility for regiocontrol in compounds having several potentially reactive sites, and multiple dehydrogenations are possible. Thus steroidal cyclohexanones can be oxidized to cyclohexadienones. (14, 89) Since secondary alcohols are oxidized to ketones with benzeneseleninic anhydride, treatment with an excess of reagent serves to convert cyclohexanols to cyclohexenones or cyclohexadienones in a one-pot reaction, a process which otherwise requires a number of steps. (89, 92, 282) These reactions can be made catalytic in selenium reagent by using various cooxidants, of which the most effective appears to be *m*-iodoxybenzoic acid.



For compounds in which the only available α position is tertiary, the principal reaction is not dehydrogenation, but α -hydroxylation. (283, 284) The balance between the two pathways can be affected by reaction conditions.

2-Methyl-1-tetralone gives mostly hydroxylation under basic conditions, but a quinone is the major product under weakly or strongly acidic conditions. (284) The dehydrogenation sometimes also fails when sensitive enones are formed. (285)



3.6. Preparation of α , β -Unsaturated Carboxylic Acid Derivatives

3.6.1.1. Selenenylation of Enolates

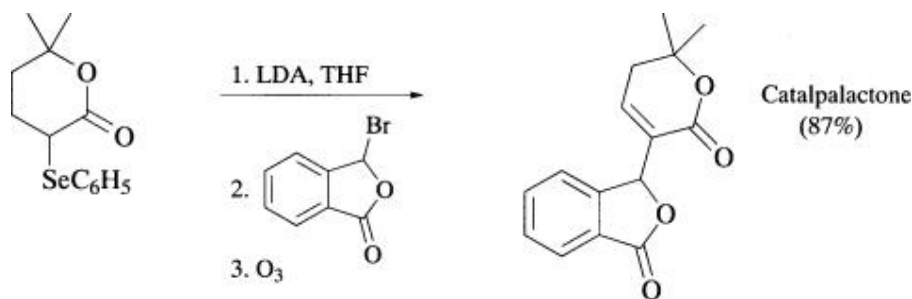
The most useful procedures for α -selenenylation of esters, lactones, amides, and lactams are reactions of the corresponding enolates with diphenyl diselenide, benzeneselenenyl chloride, or benzeneselenenyl bromide. The reactions are generally clean and proceed in high yield, though there are reports of competitive proton transfer. For example, *N*-methyl- γ -butyrolactam gives only a bis-selenide when one equivalent of lithium diisopropylamide is used, but clean monoselenenylation with two equivalents. (286, 287) Presumably in the latter case the monoselenenylated product is immediately deprotonated by excess base, so it cannot serve as a proton source for starting enolate.

3.6.1.2. Selenenylation of Silyl Ketene Acetals

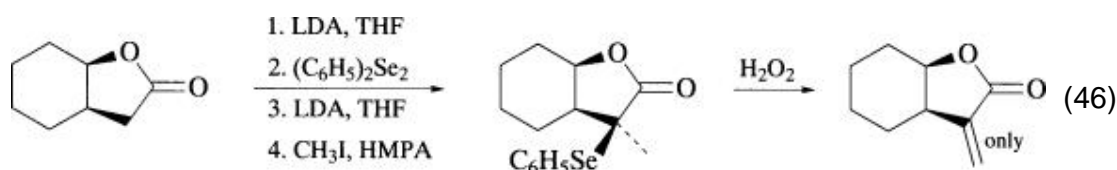
The in situ preparation of ketene acetals followed by selenenylation has been used as an alternative to direct selenenylation. (288, 289)

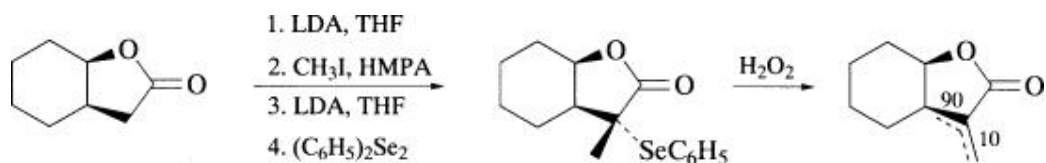
3.6.1.3. Alkylation of Selenium Substituted Enolates

The alkylation of α -phenylselenocarboxylic acids, (53, 290) amides, (290a) esters, (3, 291) and lactones (15) has been widely reported. The reaction is subject to the normal limitations of enolate alkylations: the electrophile must be a primary, unhindered iodide or other reactive S_N2 substrate. A key step in a synthesis of catalpalactone is an alkylation–selenoxide elimination sequence. (292) In this case, the alkylation of a selenium substituted enolate proceeds in higher yield than the opposite sequence of steps (alkylation of lactone followed by selenenylation). (293)

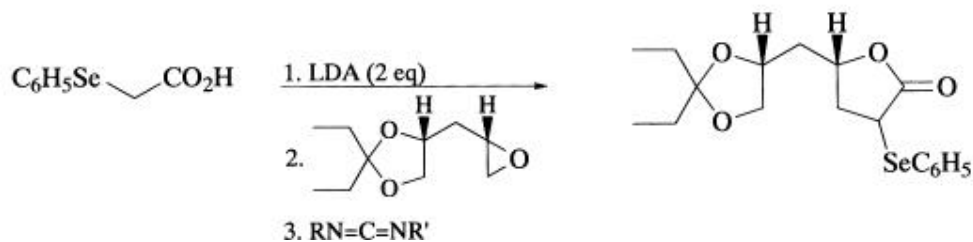
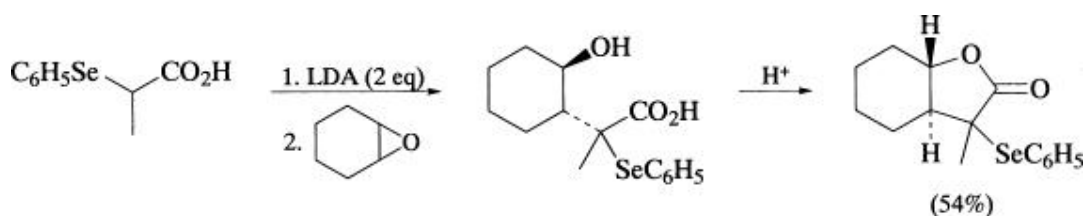


The regiochemistry of lactone dehydrogenation can be controlled by proper choice of the order in which the α -methyl and α -phenylseleno groups are introduced (Eq. 46). (15)





The dianions from α -phenylselenoacetic and α -phenylselenopropionic acids are especially nucleophilic and react with primary and even secondary epoxides to give phenylseleno- γ -lactones, (53, 290) which are precursors to α -methylenelactones and butenolides.

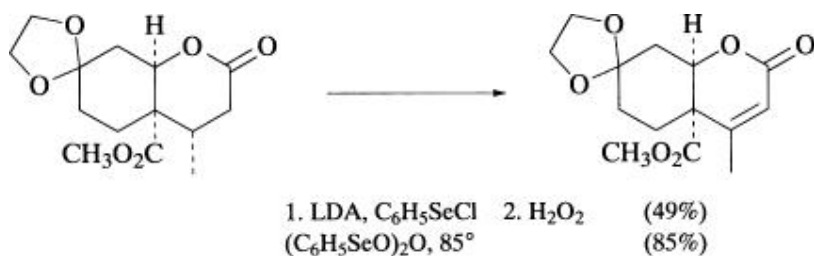


3.6.1.4. Oxidation

The oxidations of α -phenylselenocarboxylic acid derivatives exhibit fewer problems than those of ketones and aldehydes. The lower acidity of α protons inhibits several side reactions, in particular the seleno-Pummerer process.

3.6.1.5. Preparation of α , β -Unsaturated Lactones by Dehydrogenation with Benzeneseleninic Anhydride

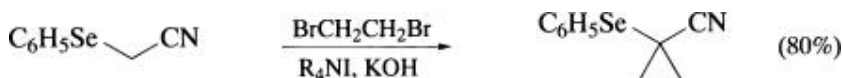
δ -Lactones can be dehydrogenated with benzeneseleninic anhydride. In one report, a better yield was obtained with this procedure than with the two-step selenenylation–oxidation sequence. (88, 294)



3.7. Preparation of α , β -Unsaturated Nitriles

3.7.1.1. Selenides

High yields in the selenenylation of metalated nitriles can be achieved only by using two equivalents of base, which avoids proton equilibration during the selenenylation step. (38) Other procedures for the preparation of phenylselenonitriles include the phase-transfer alkylation of phenylselenoacetonitrile (57) and the cyanoselenenylation of aldehydes. (37)



3.7.1.2. Oxidation

Oxidation of α -phenylselenonitriles can be carried out with any of the oxidizing agents commonly used.

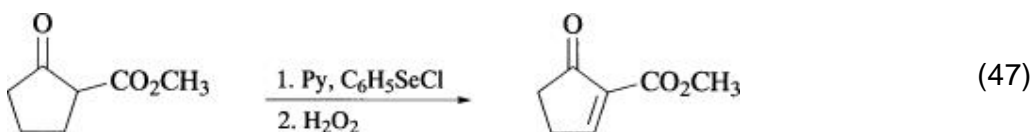
3.8. Preparation of α , β '-Unsaturated β -Dicarbonyl Compounds

The selenoxide elimination makes available for the first time a variety of unsaturated β -dicarbonyl compounds in high yield and in nonenolized form. (294a) Other methods of dehydrogenation work poorly or not at all for this class of compounds, whereas the selenenylation–selenoxide elimination procedure works particularly well for them, with often nearly quantitative yields for both steps. Previously, the most generally useful procedures involved aldol condensation–dehydration (295) and DDQ oxidation. (296)

3.8.1.1. Selenides

The high acidity and enol content of β -dicarbonyl compounds allow selenenylations to be carried out with several procedures that are not

applicable to ketones or carboxylic acids. Most commonly used is treatment with sodium hydride in tetrahydrofuran, followed by benzeneselenenyl bromide or chloride, (2) but pyridine or triethylamine can also be used as bases (Eq. 47). (97) Treatment with *N,N*-dialkylselenenamides results in clean selenenylations (Eq. 15). (64)



3.8.1.2. Oxidation

The principal precaution that must be taken to achieve high yields of β -dicarbonyl α, β '-unsaturated compounds is to protect the product from destruction by excess oxidant or by base-catalyzed polymerization, since they are often extremely sensitive to both. Hydrogen peroxide usually works well provided that exactly two equivalents are used.

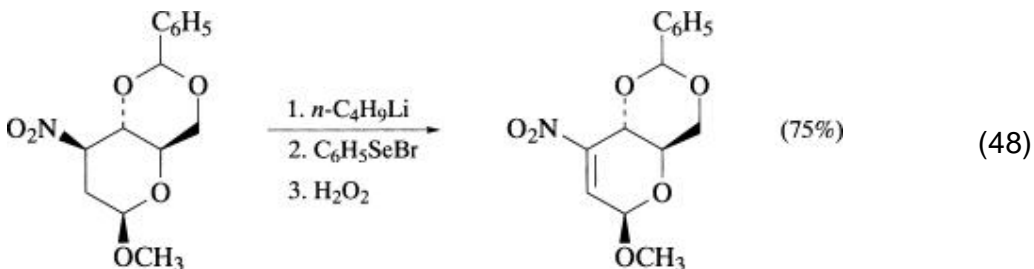
The selenoxide elimination conditions are sufficiently mild that a number of β -dicarbonyl enones which are too unstable to be isolated can be prepared and trapped in situ. Notable are a variety of *N*-benzoyl-2-acylmaleimides which are intermediates in the synthesis of cytochalasins. (172, 174, 297, 298)

3.9. Preparation of Aromatic Compounds

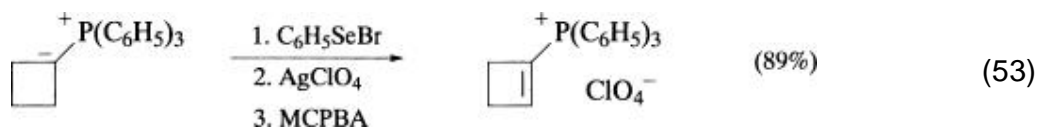
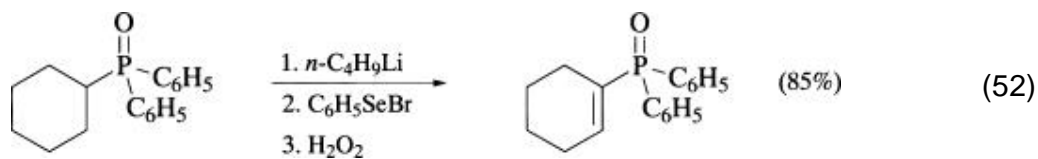
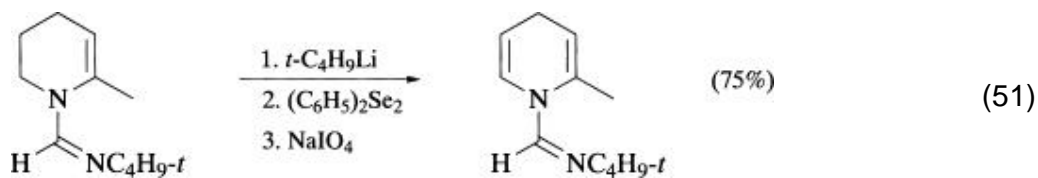
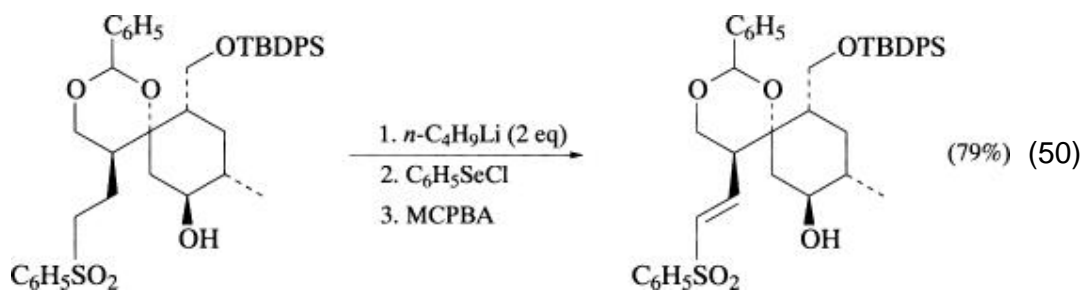
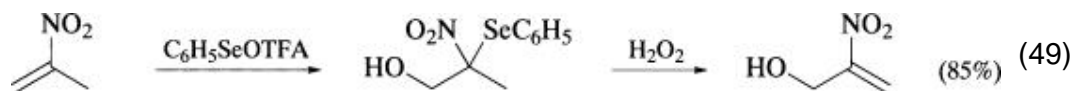
Traditional procedures for the dehydrogenation of cyclohexenones can fail with compounds having multiple functional groups. (298a) The selenoxide elimination provides a mild alternative. Since the products may be very reactive toward electrophilic substitution, it is sometimes necessary to use a selenenic acid trap. (213, 218)

3.10. Dehydrogenation of Related Compounds

Selenenylat–oxidation procedures similar to those described above can be used for the preparation of α, β -unsaturated nitro compounds (Eqs. 48 (299) and



49 (300-302)) sulfones (Eq. 50 303,303a,304) formamidines (Eq. 51 (305)), phosphine oxides (Eq. 52 (306)), phosphonium compounds (Eq. 53 (306, 307)) and phosphonates. (183) These have not been included in the tables.



4. Comparison with Other Methods

The success achieved with the selenium procedure over a number of other methods is due to the mildness of the reaction conditions, the convenience of the experimental procedures, and the reliability of the method in controlling regioselectivity. In the years immediately following introduction of the methodology, the selenoxide elimination was tried as a last resort. In recent years the selenoxide elimination is tried first, and then other methods are surveyed if it fails. Thus in earlier papers there are numerous reports of selenoxide eliminations that proceed in higher yields than other available procedures; more recently one finds examples where other procedures work better.

In the discussion below there are numerous examples of compounds for which the selenoxide elimination failed or gave poor results. In many of the cases, it is clear that optimum conditions were not used for the oxidation–elimination (in the same sense that dehydrohalogenations of α -halo ketones fail when suitable conditions are not used).

4.1. Sulfoxide Elimination

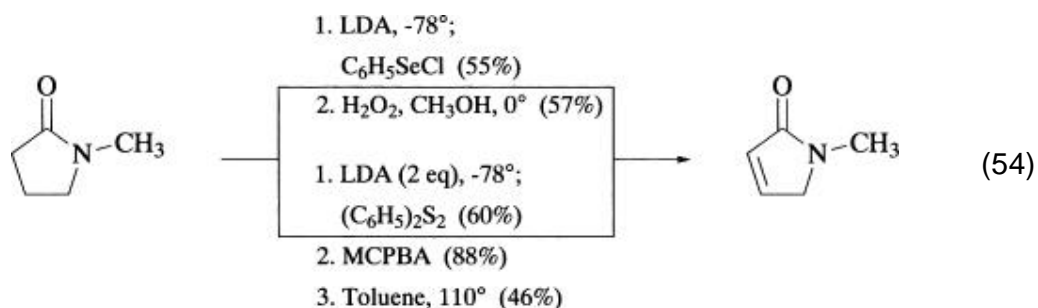
The method most like the selenoxide procedure is the analogous sulfur-based method. The advantages of the former are those of convenience, ease of preparation of the selenides, ease of oxidation, and mild conditions for all of the reactions. The sulfur reagents are less expensive and less toxic, and so disposal problems are simpler. Sulfides and sulfoxides are more stable than their selenium analogs, and can be submitted to a larger variety of reactions without damage. They are often used when the molecule containing the group is to be subjected to harsh conditions, or when the chalcogen group must survive several steps of a synthesis. (308)

The selenenyl halides are usually the reagents of choice for the introduction of selenium groups, they are shelf-stable and conveniently handled reagents. Sulfenyl halides are not, and so they are prepared just before use, or disulfides are used for the sulfenylation of enolates. This, however, results in the formation of nucleophilic lithium thiolates, which can on occasion cause problems. Disulfides do not sulfenylate stabilized enolates and so sulfenyl halides or thiol-sulfonates must be used. The introduction of sulfur groups such as methylthio and phenylthio can be done by most of the same procedures as those used for selenium, and some additional ones as well. Whereas nucleophilic substitution of α -halo carbonyl compounds with thiolates is a routine procedure, the analogous selenium procedure is restricted by the sensitivity of selenides to strong nucleophiles.

The oxidation of selenides to selenoxides proceeds cleanly with a wide variety

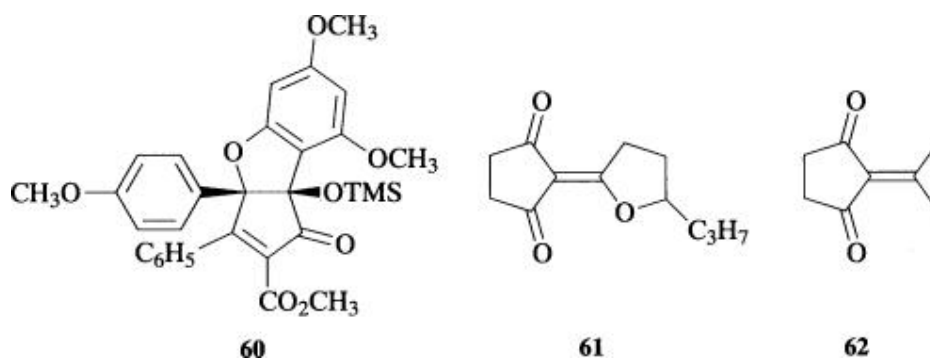
of oxidizing agents, including inexpensive ones such as hydrogen peroxide. Overoxidation to selenones is not a problem. Sulfides, on the other hand, usually require care and specialized reagents for clean oxidation to sulfoxides, since a second oxidation to sulfones occurs easily. The sulfones do not eliminate to α , β -unsaturated carbonyl compounds, and they cannot be easily reduced back to keto sulfoxides or sulfides. Selenides are more easily oxidized than sulfides, and in some cases a selenide can be oxidized in the presence of a sulfide. (181-183)

The selenoxide eliminations of ketoselenoxides typically occur between room temperature and -50° . Sulfoxides decompose at about 100° higher temperature. Thus α -methylsulfinyl ketones eliminate near 110° , α -phenylsulfinyl ketones at around 80° . Sulfoxides flanked on both sides by carbonyl groups may fragment as low as room temperature. The normal procedure for selenium is to allow selenoxide elimination to proceed during the oxidation. Sulfoxide elimination, on the other hand, is generally carried out as a separate operation, which confers some advantages: the pyrolysis conditions are more easily optimized since potentially interfering species present as a result of the oxidation step are removed by workup, and different solvents can be easily used for oxidations and eliminations. In addition, sulfoxides can be purified; this can be more difficult for selenides or sulfides since their polarity differs little from that of the starting carbonyl compound or product α , β -unsaturated carbonyl compound. Chemical manipulations of ketoselenoxides is almost never done, whereas sulfoxides have a rich chemistry. Furthermore, sulfoxides are configurationally stable, and so enantiomerically pure sulfoxides can be used for asymmetric syntheses; such applications are unknown for selenoxides because of their chemical and configurational instability. In most cases where data for both selenoxide and sulfoxide eliminations were run on the same compound, comparable yields were obtained. Equation 54 illustrates and compares the typical conditions used for the two procedures. The use of disulfide as sulfenylating agent (rather than the selenenyl halide), the use of MCPBA as oxidizing agent (rather than hydrogen peroxide), isolation and purification of the intermediate sulfoxide, and pyrolysis in refluxing toluene (compared to 0 – 25°) are typical conditions used which differ from those used for selenium. (286, 309)



There have been several reports of compounds where the selenoxide elimination fails or gives a significantly poorer yield than the sulfoxide elimination. For compound **60**, (310) an intermediate in the synthesis of rocaglamide, the selenenylation–dehydroselenenylation fails, but sulfoxide elimination proceeds in 72% yield. Compound **61** (311) could not be selenenylated. However, sulfenylation succeeded with *N*-phenylthiophthalimide (70% yield), and the sulfoxide elimination occurred in 27% yield. The selenide precursor for the related compound **62** (220) could be prepared, but oxidation gave little of the enone. Sulfoxide elimination proceeded well.

α -Phenylseleno ketone tosylhydrazones can be prepared, but oxidation with several reagents did not produce α , β -unsaturated tosylhydrazones. Apparently the

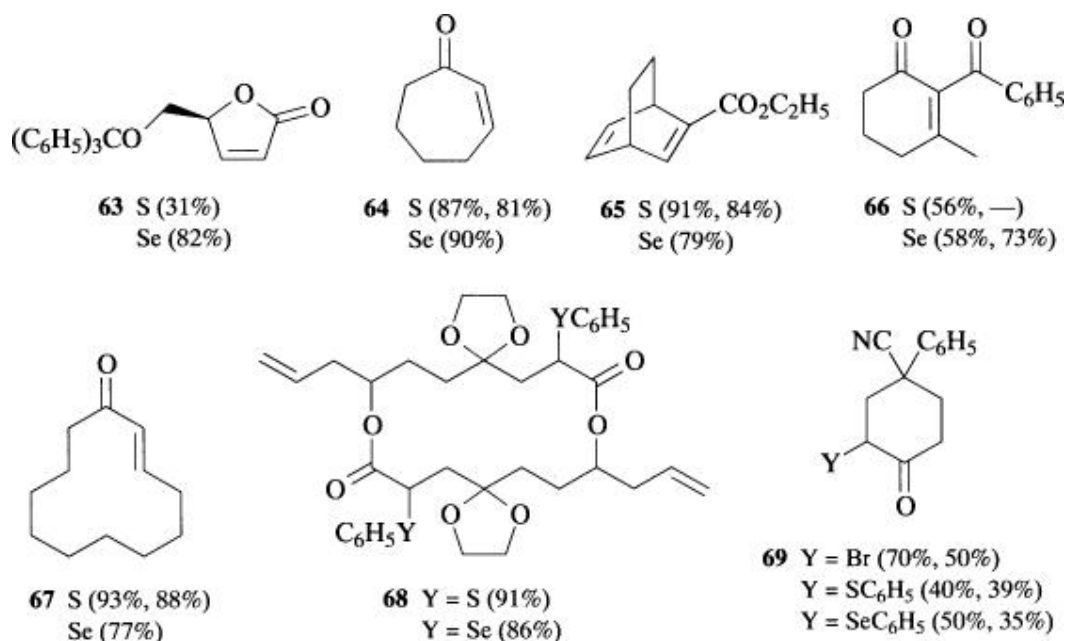


imine group is oxidized faster than the selenide. (312) The problem was solved by converting the α -phenylsulfino ketone to the tosylhydrazone and thermolyzing it.

There are also cases where the milder conditions of selenoxide elimination allow the synthesis of α , β -unsaturated carbonyl compounds for which the sulfoxide elimination fails. Compound **46** is very easily polymerized, and oxidation of the precursor sulfide could not be achieved without destruction of the product or starting material. Selenoxide elimination provided solutions of **46** which could not be concentrated, but could be observed spectroscopically. (176)

An interesting contrast is provided by the sulfoxide and selenoxide procedures for preparing nonracemic **63** (168a) (where two yields are given, the first represents introduction of PhSe/PhS/Br). Not only does the sulfoxide procedure give lower yields, the harsher reaction conditions lead to partial racemization of the product (the selenoxide product is 100% optically pure, the

sulfoxide only 60%). Other components where comparable selenoxide and sulfoxide eliminations were carried out are **64**, (2, 6) **65**, (2, 6) **66**, (313) **67**, (3, 6) and **68**. (308) The last produced the *cis* diene diolide. For the elimination of H-Y in **69**, dehydrohalogenation gives the best yield, sulfur and selenium are comparable. (314)

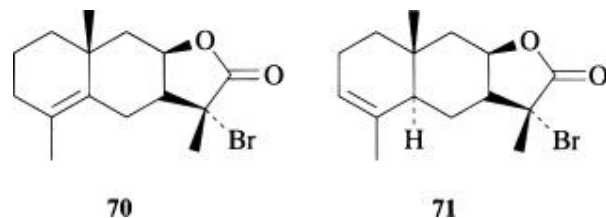


4.2. Halogenation–Dehydrohalogenation

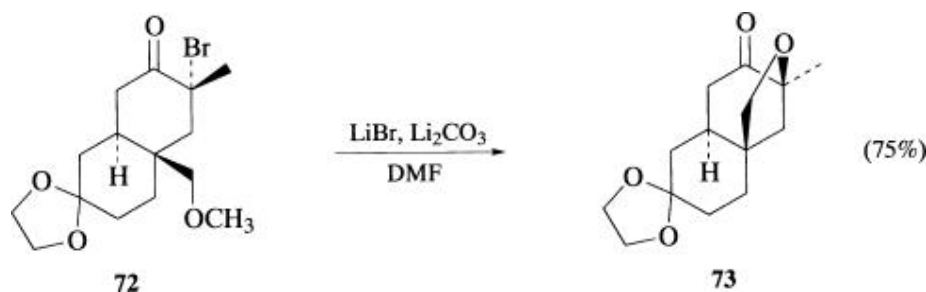
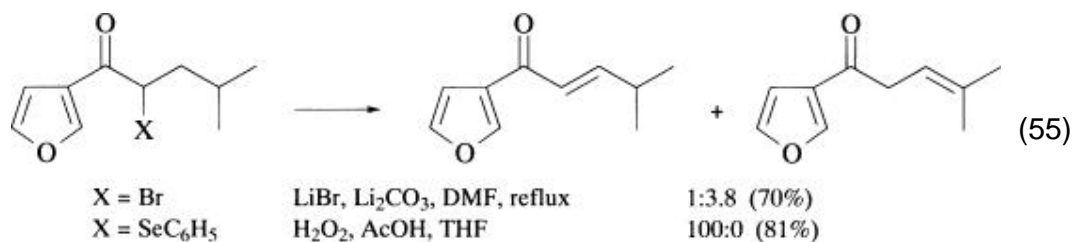
The bromination of carbonyl compounds followed by base-induced dehydrobromination was the principal procedure used for the dehydrogenation of carbonyl compounds before the introduction of sulfur and selenium methodology. When proper conditions, such as a weak base (lithium bromide, lithium carbonate) in a dipolar aprotic solvent at high temperature, are used, and if the substrates are relatively simple compounds, excellent yields can be obtained. (315) The reaction is capricious, however, and the harsh conditions frequently result in low yields, decomposition of starting material or product, or loss of regiochemical control. A related procedure is the bromination–dehydrobromination of ketals, (316, 317) and this is sometimes still the method of choice when the selenoxide elimination fails (e.g., synthesis of codeine (193)).

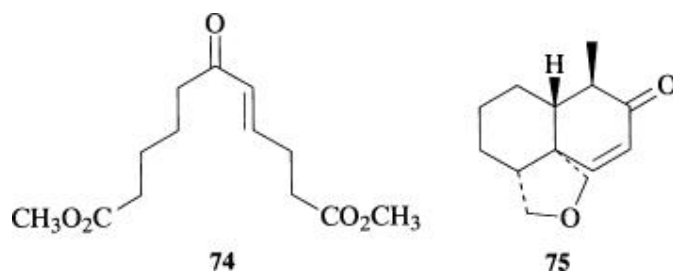
For molecules with any degree of complexity, the selenoxide elimination and the Saegusa oxidation have largely supplanted dehydrohalogenation. There are still occasions when dehydrohalogenation can perform a useful role, such as when the *anti*-elimination stereochemistry of the dehydrohalogenation produces a different regioisomer than the *syn* elimination of a selenoxide.

(318-320) For example, the selenenylation–oxidation of *cis*-fused γ -lactones produces mostly endocyclic butenolides. The dehydrobromination of **70** works poorly (DBU in toluene, <10% yield) but that of **71** is more successful, giving the α -methylene lactone in 46% overall yield. (319)

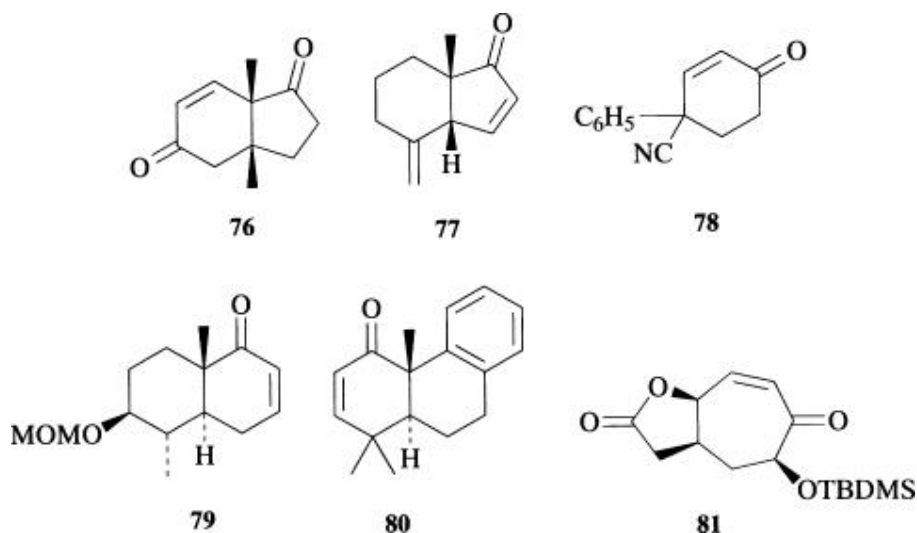


The high temperatures and long reaction times of typical dehydrohalogenation procedures result in a number of side reactions. A simple example is given in Eq. 55, in which a mixture of isomeric olefins is formed. (321) The attempted dehydrohalogenation of **72** produces the cyclic ether **73** and less than 1% of the desired enone (selenenylation-oxidation worked in 95% yield). (49) Selenium methodology is superior to bromination–dehydrobromination for compounds **11** and **12**, (40) **74**, (322) and **75**. (323) Attempts to make enones in the peristylane series (**52**) by dehydrobromination were not successful, but selenoxide elimination works well. (179)





There have, nevertheless, been several reports of bromination–dehydrobrominations that work where the selenoxide elimination gives poorer results. Compound **76** (324) is formed in 66% yield, sulfur or selenium reagents give poorer results. For **77** (325) both the selenium method and the Saegusa oxidation of the enol silyl ether fail, and bromination–dehydrobromination works in 77% yield. For the preparation of **78**, DABCO–triethylamine dehydrohalogenation of the α -bromoketone works in 50% yield, the selenium method in 35%, and sulfur in 39% yield. (314) Dehydrobromination with DBU gives **79** in 83% yield; the selenium method does not work. (326) For **80** the selenium (66%) and bromine (72%) methods work comparably. (327) All of these cases involve systems known to give problems when the α -keto selenide is oxidized with hydrogen peroxide. Although the oxidation conditions were only given for **81** (40% for selenium using hydrogen peroxide, 73% for bromine), (269) it is likely that better results would be obtained for most if not all of these compounds if optimum conditions were used.



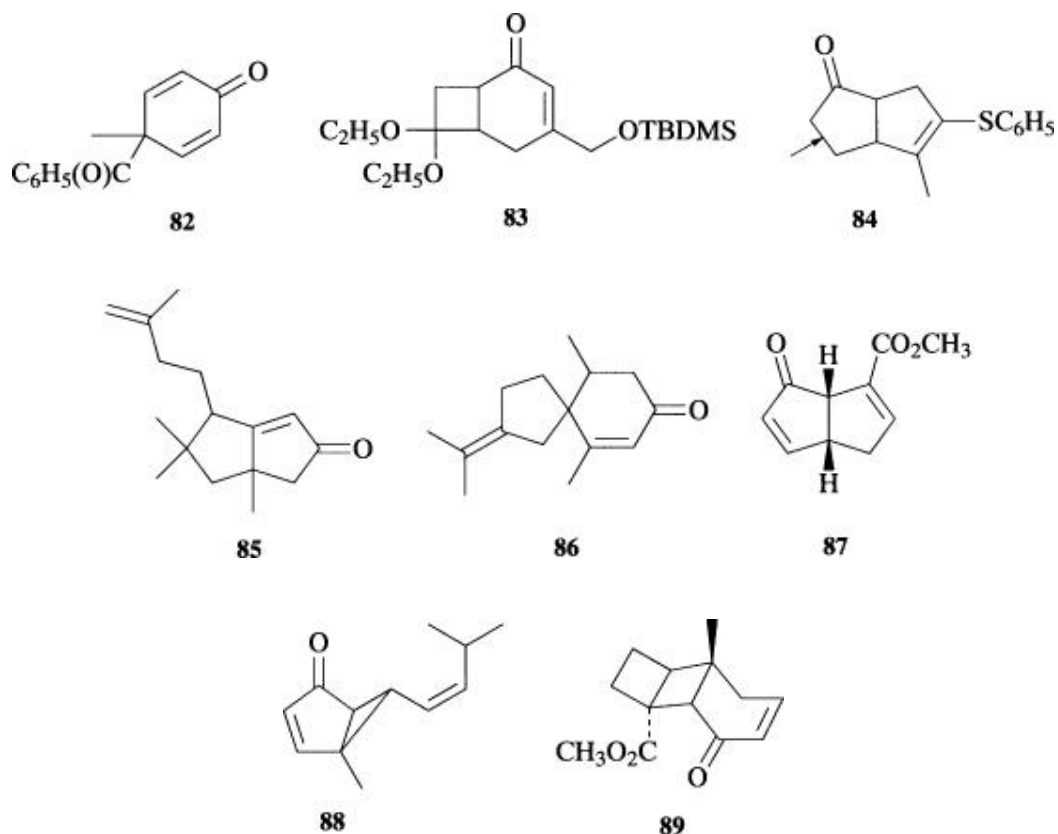
4.3. Other Elimination Reactions

Acetate pyrolysis had been used to make α , β -unsaturated carbonyl compounds, (328, 329) but the starting materials are not readily available, and the conditions are too harsh for general use with complex molecules. The reaction of a β -keto ester enolate with thionyl chloride produces enone in slightly better yield (64%) than that provided by the selenoxide route (56%). (330)

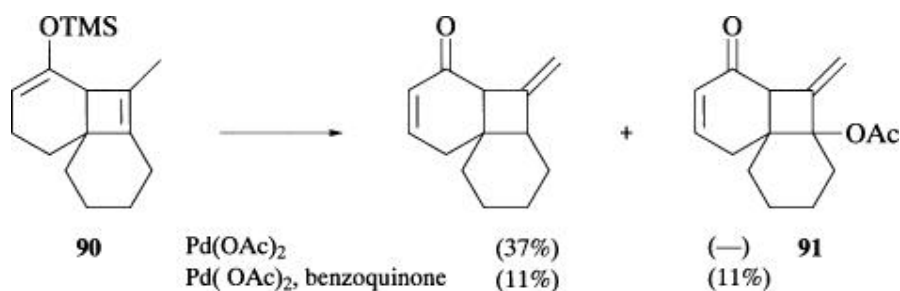
4.4. Saegusa Oxidation

The reaction of enol silyl ethers with palladium(II) acetate produces enones. The reaction requires essentially stoichiometric amounts of palladium, and therefore is expensive for large-scale work. Benzoquinone is sometimes used to reoxidize the palladium salts, but at most two turnovers can be achieved in this way. (331) However, the mild conditions of the Saegusa oxidation and its high tolerance for other functional groups have made it the most frequently used alternative when the selenoxide elimination fails.

The cyclohexadienone **82** is not obtained in pure form by selenoxide elimination under a variety of conditions. Oxidation of the appropriate enol silyl ether with stoichiometric palladium(II) acetate is more effective. (332, 333) The strained cyclohexenone **83** could not be formed by selenoxide elimination, but oxidation of the enol silyl ether with Pd(OAc)₂/benzoquinone produced **83** in 39% yield. (58) Resistance to incorporation of additional trigonal carbon atoms into the strained ring system is similar to what is seen in the D-ring of steroids (see section on **Preparation of α , β -Unsaturated Ketones**). When the selenoxide elimination process fails it is usually because something goes awry in the oxidation–elimination step, but occasionally the selenenylation can be the problem. For example, clean sulfenylation or selenenylation could not be achieved with **84**, but Saegusa oxidation worked in 69% yield. (334) The compounds **85**, (335) **86**, (336) **87**, (225) **88**, (337) and **89** (338) are also formed in higher yield with the Saegusa oxidation than by selenoxide elimination, sulfoxide elimination, and/or bromination–dehydrobromination.

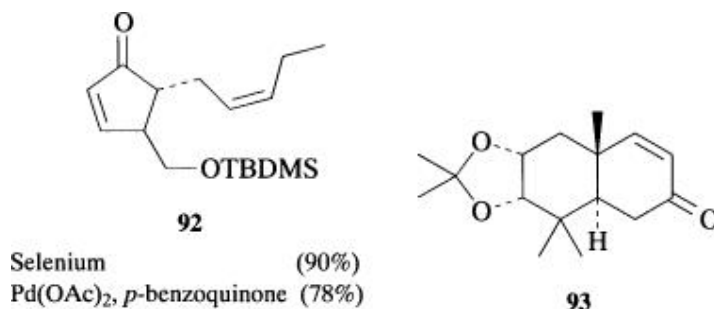


Palladium oxidation can result in side reactions of several types. For example, the enol silyl ether **90** gives enone in 37% yield, although double bond isomerization also occurs. Selenoxide elimination works even less well (20%) but was not done under optimum conditions. Furthermore, when benzoquinone is used as co-oxidant, the acetoxyated product **91** is formed. (339)



In other cases the results for selenium-based procedures are comparable or superior (e.g., **92**). (249) The preparation of **93** by using selenium methodology

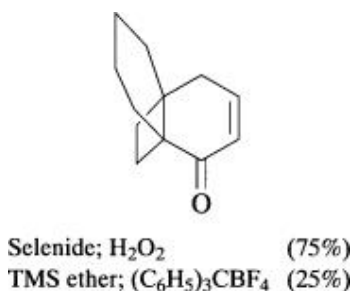
(49%) is better than either the Saegusa oxidation or bromination-dehydrobromination. (340)



A method related to the Saegusa oxidation is the reaction of enol acetates or enol silyl ethers with catalytic Pd(OAc)₂ using allyl carbonate as oxidant. (341) α , β -Unsaturated ketones, aldehydes, and lactones have been prepared this way. Although yields are comparable to those obtained by the Saegusa oxidation or the selenium methodology, the reaction has not been used very extensively.

4.5. Oxidation of Enol Silyl Ethers with Trityl Fluoroborate (342)

In one case where this procedure was compared with a selenoxide elimination the latter was much superior. (343)

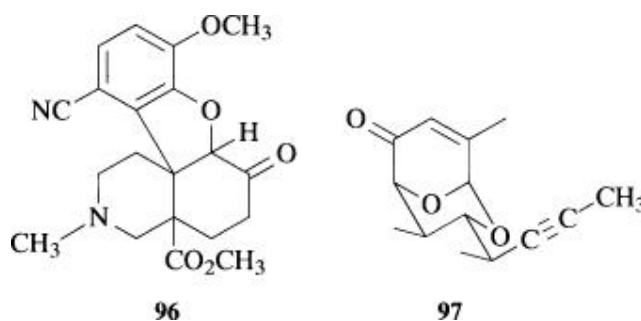
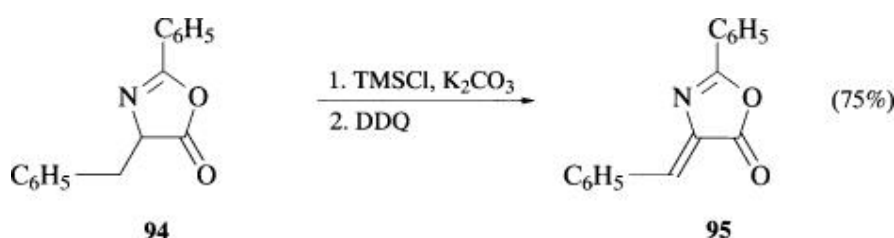


4.6. Oxidation with Selenium Dioxide

The selenium dioxide oxidation is occasionally used to perform dehydrogenations, although other procedures have largely supplanted it. The reaction is erratic and produces hard-to-remove selenium-containing byproducts. No examples have been found for which selenium dioxide oxidation gives better results than does the selenoxide elimination. Where comparison has been made, selenium dioxide generally works much less well. (86)

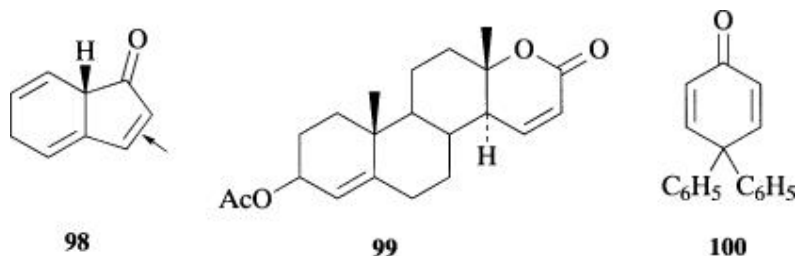
4.7. Oxidation with Dicyanodichloroquinone (DDQ) and Other Quinones

The DDQ procedures can give high yields of α , β -unsaturated carbonyl compounds. It appears to be especially effective for the dehydrogenation of β -dicarbonyl compounds, and is the only method other than the selenoxide and sulfoxide eliminations that works consistently with them. (296) Some specialized systems actually work better with DDQ than by selenoxide elimination. Compound **94** was subjected to a variety of dehydrogenating conditions including bromination/dehydrobromination, selenenylation/oxidation, and Saegusa oxidation. The best yield of **95** is obtained by oxidation of the enol silyl ether with DDQ. (344) The tertiary amine **96** can be selenenylated, but oxidation with *m*-chloroperoxybenzoic acid does not give enone. Bromination/dehydrobromination does not work either. Acid-catalyzed oxidation with DDQ



under carefully optimized conditions produces enone in 70% yield. (192) Whereas formation of enone **97** by selenoxide elimination or oxidation with benzeneseleninic anhydride works fairly well (55%), the best procedure is oxidation of the enol silyl ether with DDQ (80%). (345)

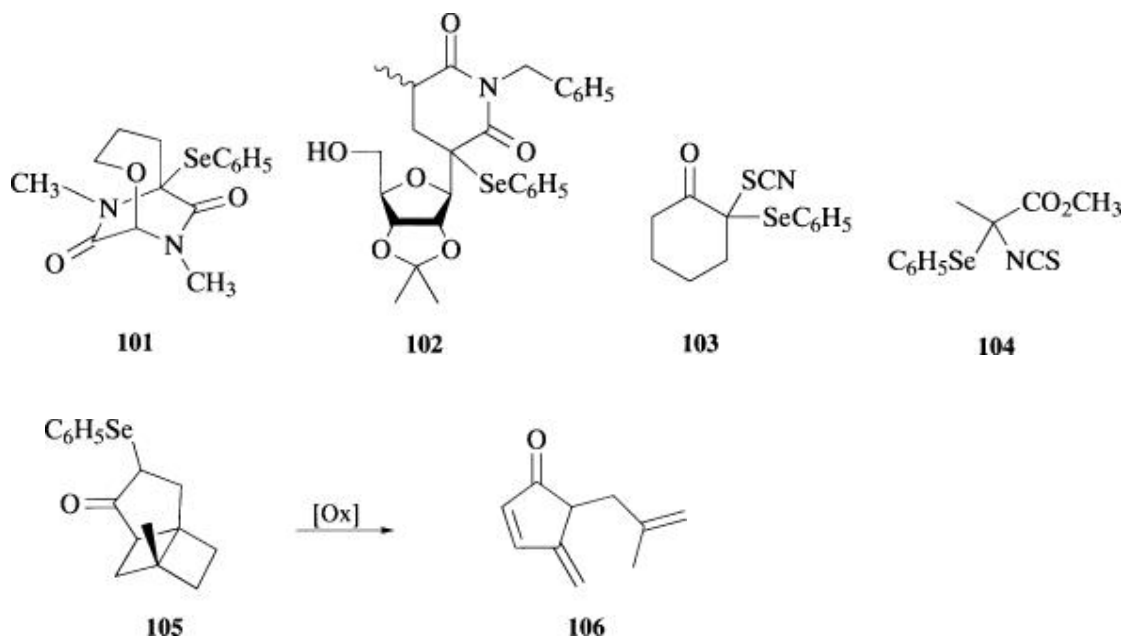
A number of unsuccessful oxidations with DDQ have been reported, for which selenium based procedures gave satisfactory results: **98**, (285) **99**, (86) and **100** (chloranil and selenium dioxide did not work, selenium gave 92% yield). (346)



4.8. Compounds that Could not be Dehydrogenated

Some selenides do not produce useful yields of olefins upon oxidation. Selenide **101** (60) gives products in which OH (36%) and OOH (41%) replaced the phenylseleno group. A carbonium ion mechanism was proposed. The compound with one less CH₂ in the bridge gives a stable selenoxide (days at reflux, but solvent not specified).

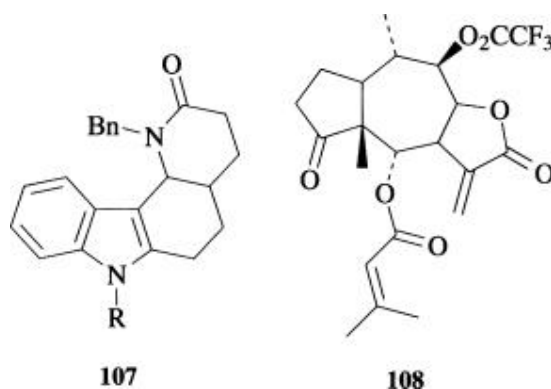
Oxidation of **102** with *m*-chloroperoxybenzoic acid, hydrogen peroxide, or ozone does not give isolable products. (147) Neither the α -phenylselenothiocyanate **103** (155) nor the isothiocyanate **104** (154) produces α, β -unsaturated carbonyl compounds. For the latter, a variety of conditions for the oxidation and elimination were tried. The tricyclic ketoselenide **105** can be prepared smoothly, but oxidation gives only the fragmented enone **106**. (347)



We believe that full consideration of the chemistry of the intermediate

selenoxides as described in this chapter would result in the development of suitable conditions for successful oxidation–fragmentation of some if not most of the selenides, as well as those discussed in the previous sections on alternative methods.

Compound **107** (348) could not be sulfenylated or selenenylated—apparently preparation of the enolate failed. Compound **108** could not be selenenylated. Bromination worked, but no cyclopentenone could be isolated after attempted dehydrobromination. (98)



5. Experimental Conditions

CAUTION: organoselenium compounds are toxic, and care should be taken to avoid exposure. Although few of the selenium compounds encountered are volatile enough to constitute a significant inhalation problem, reactions involving organo-selenium compounds should be carried out only in a well-ventilated hood, and skin contact should be avoided. The authors are aware of no cases where laboratory workers suffered ill effects while carrying out selenium reactions of the type discussed in this chapter. Exposure to trace amounts of selenium does not pose a chronic toxicity problem (such as encountered with the heavy metals lead, mercury, and cadmium) since selenium is an essential element for all higher organisms, and is a necessary constituent of a normal diet (minimum daily requirements are in the 100- to 500- μg range).

5.1.1.1.1. Selenenylation

Use the reaction of benzeneselenenyl chloride with enol silyl ethers when these are available. If the enolate is being used, add selenenyl halide rapidly at low temperature to avoid equilibration. There are many reports of warming to room temperature to “complete” the selenenylation, but in most cases this can only do harm, since the selenylation is usually rapid even at -78° .

5.1.1.1.2. Oxidation–elimination

Use the least polar solvents available: methylene chloride or carbon tetrachloride are excellent. Use hydrogen peroxide for uncomplicated systems: that is, acyclic secondary or tertiary selenides, and cyclic tertiary selenides without much ring strain for which no seleno-Pummerer reaction is possible.

For difficult systems use ozone or *m*-chloroperoxybenzoic acid oxidation at low temperature followed by pyrolysis under mildly basic conditions, with a selenenic acid trap for especially problematic cases. Difficult systems involve secondary selenides with an easily enolizable α hydrogen, cyclic compounds where ring strain is increased by introduction of the double bond, compounds where the C - Se and C - H bonds cannot easily achieve coplanarity (6-, 7-, and 8-membered rings), or compounds with carbonium ion stabilizing groups (O, N) on the carbon bearing the seleno group.

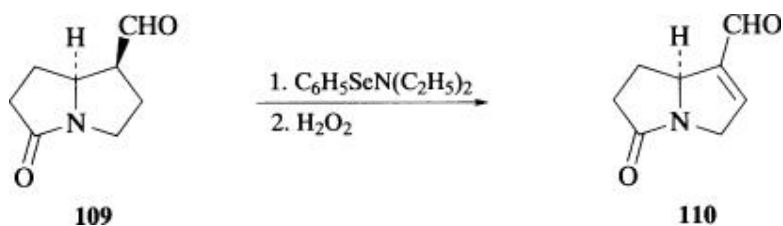
The elimination of selenoxides produces a 1:1 molar ratio of benzeneseleninic acid and diphenyl diselenide. If oxidation of the selenide is carried out at temperatures where selenoxide elimination also occurs, two equivalents of oxidant may be required to complete the oxidation.

5.1.1.1.3. Recovery of Diphenyl Diselenide

Under typical conditions involving excess hydrogen peroxide as oxidant

diphenyl diselenide is oxidized to benzeneseleninic acid. Removal of the seleninic acid is usually accomplished by base extraction; seleninic acids behave much like carboxylic acids in this respect. Benzeneseleninic acid slowly degrades when left in contact with hydrogen peroxide, and should therefore be recovered promptly. The base extract can be treated with one of several reducing agents (e.g., sodium thiosulfate (2) or sodium dithionite (89)) to recover diphenyl diselenide in high yield (see [Experimental Procedures](#)).

6. Experimental Procedures



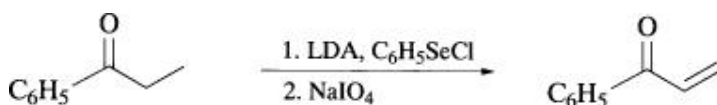
6.1.1.1. 5-Aza-6-oxobicyclo[3.3.0]oct-2-ene-2-carboxaldehyde (**110**)

[Selenenylation of an Aldehyde with a Selenenamide (Method A-2)] (349)

To a stirred solution of the aldehyde **109** (300 mg, 1.96 mmol) in 10 mL of THF at room temperature was added *N,N*-diethylbenzeneselenamide (1.1 g, 4.4 mmol) in one portion. The solution was stirred for 16 hours, and concentrated to a brown oil. The oil was chromatographed over silica gel, eluted with 20% THF-hexanes to give 488 mg (81%) of orange crystalline solid 2-formyl-2-phenylseleno-5-azabicyclo[3.3.0]octan-6-one (mp 115–117°).

$R_f = 0.3$ in 50% THF-hexanes, IR (neat) 1705, 1685 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 9.8 (s, 1 H), 7.4 (m, 5 H), 4.3 (m, 1 H), 3.75 (m, 1 H), 3.15 (m, 1 H), 2.7 (m, 2 H), 2.35 (m, 2 H), 2.15 (m, 1 H), 1.95 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 191.1, 174.3, 137.6, 129.6, 128.0, 119.5, 67.9, 64.1, 40.2, 31.8, 25.6; mass spectrum m/z (rel. intensity) 309 (2.9), 152 (62.2), 124 (14.8), 97 (61.5), 83 (100), 69 (16.3).

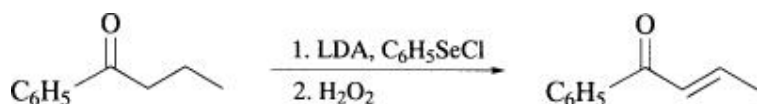
The selenide (400 mg, 1.3 mmol) was dissolved in 20 mL of THF, and to this was added 30% hydrogen peroxide (3 mL, 6.1 mmol). The mixture was stirred overnight, then the solvent was removed and the residue chromatographed over silica gel THF-hexanes to give 185 mg (95%) of **110** as an oil; IR (neat) 1710, 1660 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 9.85 (s, 1 H), 6.9 (dd, $J = 2, 14$ Hz, 1 H), 4.9 (m, 1 H), 4.65 (m, 1 H), 3.9 (m, 1 H), 2.7 (m, 1 H), 2.4 (m, 1 H), 1.9 (m, 1 H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.1, 178.7, 146.2, 136.9, 66.3, 65.2, 33.5, 29.8; mass spectrum m/z (rel. intensity) 151 (76.7), 122 (31.8), 96 (50.2), 68 (58.9), 55 (94.6); exact mass calcd for $\text{C}_8\text{H}_9\text{NO}_2$ (M^+) 151.0634, found 151.0640.



6.1.1.2. 1-Phenyl-2-propen-1-one [Selenenylation of a Ketone Enolate (Method A-1), Oxidation with Sodium meta-Periodate] (2)

The following serves as a typical procedure for the preparation of an α -phenylseleno ketone from the lithium enolate. Into a 50-mL two-necked round-bottomed flask (magnetic stirrer, septum, 10-mL addition funnel) was distilled 20 mL of THF under nitrogen. The flask was cooled to -78° , and 0.92 mL (6.0 mmol) of diisopropylamine was added, followed by 2.94 mL of 2.05 M *n*-butyllithium in hexane. A solution of propiophenone (0.67 g, 5 mmol) in 2 mL of THF was added dropwise, and the solution was stirred for 15 minutes. Into the addition funnel was placed 0.94 g (3.0 mmol) of diphenyl diselenide, and this was dissolved in 2 mL of THF. Bromine (0.162 mL, 0.48 g, 3.0 mmol) was added dropwise to the solution, which was agitated briefly to dissolve any $C_6H_5SeBr_3$ formed. The benzeneselenenyl bromide solution was added rapidly to the enolate solution (immediate decolorization), and the cold reaction mixture was poured into 50 mL of 0.5 N HCl and 40 mL of 50% ether-pentane. The organic layer was washed with water, saturated sodium bicarbonate solution, and brine and dried by filtering through a cone of anhydrous sodium sulfate. Solvent was removed, and the crude product was crystallized from ether-pentane at -20° (0.87 g, mp $36.5\text{--}37^\circ$). Chromatography of the mother liquor gave a further 0.40 g, isolated by crystallization (total yield 1.27 g, 87%): 1H NMR δ 1.60 (d, $J = 7.0$ Hz, 3 H), 4.58 (q, $J = 7.0$ Hz, 1 H), 7.1–7.6 (m, 8 H), 7.88 (m, 2 H); IR 1680, 1598, 1582 cm^{-1} . Anal. Calcd for $C_{15}H_{14}OSe$: C, 62.29; H, 4.88. Found: C, 62.23; H, 4.95.

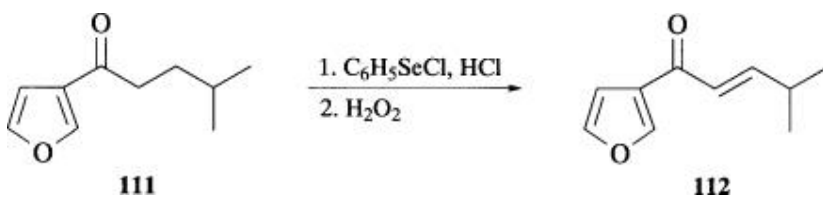
To a solution of 1.00 g (3.46 mmol) of 1-phenyl-2-phenylseleno-1-propanone in 60 mL of methanol was added 10 mL of water, 0.35 g (4 mmol) of sodium bicarbonate, and 1.72 g (8 mmol) of $NaIO_4$ with vigorous stirring. After 90 minutes at 25° , the reaction mixture was poured into 40 mL of 15% ether-pentane and 40 mL of saturated sodium bicarbonate solution. The organic layer was washed with water and brine. A few crystals of hydroquinone were added, solvent was removed, and the residue was distilled (0.2 mm, receiver at -20°), giving 404 mg (89%) of **1-phenyl-2-propen-1-one**, with no detectable impurities by 1H NMR δ 5.84 (dd, $J = 2.2, 10.7$ Hz, 1 H), 6.39 (dd, $J = 2.2, 17.3$ Hz, 1 H), 7.16 (dd, $J = 10.7, 17.3$ Hz, 1 H), 7.4–7.6 (m, 3 H), 7.92 (dd, $J = 2, 8$ Hz, 2 H); IR 1672, 1664, 1610, 1597 cm^{-1} .



6.1.1.3. *trans*-1-Phenyl-2-buten-1-one [Oxidation with Hydrogen Peroxide] (2)

Following the selenide preparation outlined in the experiment above, 2.96 g (20 mmol) of *n*-butyrophenone gave 5.00 g (82%) of 1-phenyl-2-phenylseleno-1-butanone after slow crystallization at -24° from 25 mL of 50% ether-pentane: mp $50.5\text{--}52.5^{\circ}$; $^1\text{H NMR } \delta$ 1.01 (t, $J = 6.9$ Hz, 3 H), 1.6–2.2 (m, 2 H), 4.30 (t, $J = 7.2$ Hz, 1 H), 7.0–7.5 (m, 8 H), 7.77 (m, 2 H); IR 1678, 1599, 1581 cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{OSe}$: C, 63.37; H, 5.32; Se, 26.04. Found: C, 63.45; H, 5.28; Se, 25.86.

Into a 250-mL three-necked round-bottomed flask equipped with a dropping funnel, condenser, and thermometer was added a solution of 4.55 g (0.015 mol) of selenide in 50 mL of dichloromethane containing 2.42 mL (0.03 mol) of pyridine. To the stirred solution was gradually added 0.04 mol of hydrogen peroxide (4.53 g of 30% hydrogen peroxide in 4 mL of water), with cooling by an ice-salt bath to keep the temperature between 30 and 35° (**CAUTION: the reaction is strongly exothermic**). The reaction mixture was stirred vigorously at 25° for an additional 15 minutes after removing the bath and then was added to 25 mL of dichloromethane and 30 mL of 7% sodium bicarbonate solution. The aqueous layer was washed with 25 mL of dichloromethane, and the combined organic layers were washed with 30 mL of 10% HCl solution and 30 mL of saturated brine and dried (sodium sulfate). After solvent removal, distillation gave 2.02 g (92%) of *trans*-enone: bp $84\text{--}85^{\circ}$ (0.5 mm); $^1\text{H NMR } \delta$ 1.89 (d, $J = 5.2$ Hz, 3 H), 6.72–7.15 (m, 2 H), 7.4 (m, 3 H), 7.84 (m, 2 H).

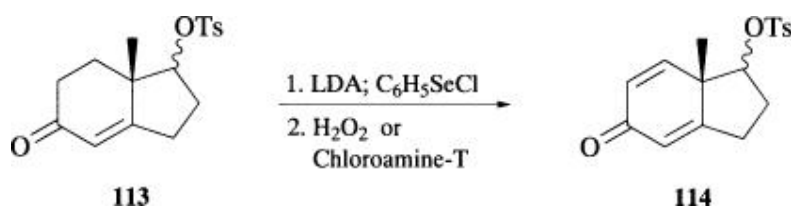


6.1.1.4. Isoegomaketone [**112**, *trans*-1-(3-furyl)-4-methylpent-2-en-1-one] [Acid-Catalyzed Selenenylation of a Ketone (Method A-2), Oxidation with Hydrogen Peroxide] (321)

To benzeneselenenyl chloride (Aldrich Chemical Co.) (51 g, 0.266 mol) was added ethyl acetate (1000 mL) and **111** (37 g, 36.3 mL, 0.233 mol). Concentrated HCl (4 mL) was added and the solution was stirred magnetically for 60 hours at room temperature. The light yellow to orange solution was then washed with water (3×200 mL), sodium bicarbonate (saturated, 2×200 mL) and dried (molecular sieves, type 3A), and the solvent was removed under reduced pressure. Several crystallizations from minimal cold (0°) petroleum ether afforded 65 g (92%) of white crystalline 1-(3-furyl)-2-phenylseleno-4-methylpentan-1-one: mp $59\text{--}60^{\circ}$; IR (Nujol) 3120

and 1640 cm^{-1} ; $^1\text{H NMR}$ (CCl_4) δ 0.85 (2 d, 6 H, 2 CH_3), 1.70 (m, H, CHMe_2), 3.95 (t, H, CHCO), 6.60 (s, H, H-4), 7.23 (m, 6 H, H-5 and PhSe), 7.67 (s, H, H-2). The chemical ionization mass spectrum $M + 1$ peak occurred at 323, but peaks corresponding to the other selenium isotopes were also observed. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{SeO}_2$: C, 60.00; H, 5.35; Se, 24.65. Found: C, 59.82; H, 5.56; Se, 24.41.

The crystalline selenide (58.8 g) was dissolved in THF (400 mL) and ethyl acetate (400 mL) and cooled to 5° . Glacial acetic acid (3 mL) was added followed by the dropwise addition of hydrogen peroxide (30%, 56 mL), whose exothermic reaction requires keeping the temperature below 35° . After 4 hours, the magnetically stirred solution was washed with sodium bicarbonate and brine (saturated, $3 \times 200\text{ mL}$ each), dried (magnesium sulfate), and evaporated under reduced pressure to afford 27.6 g (92%) of crude isoegomaketone (**112**). One impurity, indicated by the IR peak at 1700 cm^{-1} , does not readily elute from silica gel with dichloromethane; a bright yellow, but trace, contaminant elutes just prior to the isoegomaketone. The pure, water-white elution product was distilled, bp 58° (0.08 mm Hg), to give 24.6 g (81% yield): IR (neat) 3130, 2960, 1665, 1618, 1556 cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 1.08 (d, 6 H, 2 CH_3 , $J = 7\text{ Hz}$), 2.48 (m, 2 H [*sic*], CH, $J = 7\text{ Hz}$), 6.46 (d, 1 H, COCH, $J = 16\text{ Hz}$), 6.98 (d, 1 H, $J = 7$ and 16 Hz), 6.76 (s, 1 H, H-4, $J = 2\text{ Hz}$), 7.40 (s, 1 H, H-5, $J = 2\text{ Hz}$), 8.06 (s, 1 H, H-2). Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.14; H, 7.37. Found: C, 72.97; H, 7.49.



6.1.1.5. *7a-Methyl-1-(4-methylphenylsulfonyloxy)-indan-5(6H)-one* (**114**)
[Selenenylation of a Dienolate with Benzeneselenenyl Bromide, Oxidation with Hydrogen Peroxide or Chloramine-T] (214)

Tosylate **113** (200 mg, 0.625 mmol) was dissolved in dry THF (15 mL) in a dry flask under nitrogen and cooled to -78° , and lithium diisopropylamide (0.81 mmol) [from *n*-butyllithium (1.6 M; 0.5 mL, 0.81 mmol) and diisopropylamine (82.06 mg, 113.6 μL , 0.81 mmol)] in THF (5 mL) was then added. The solution was stirred for a further 0.5 hour and benzeneselenenyl bromide (0.34 mmol) [from diphenyl diselenide (107 mg, 0.34 mmol) and bromine (55 mg, 18 μL , 0.34 mmol)] in THF (5 mL) was added. The solution was then allowed to warm to room temperature during 1 hour, poured into 0.5 M HCl (50 mL) and extracted with ether ($3 \times 50\text{ mL}$). The organic phase

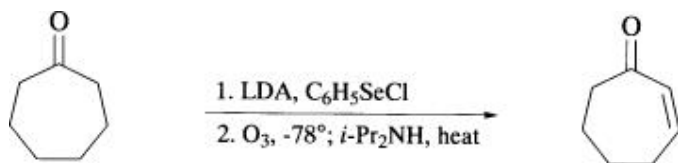
was washed with water (2 × 20 mL), dried (sodium sulfate), and the solvent was removed under reduced pressure to give a yellow solid which was chromatographed to give the starting material (**113**) (39 mg, 19%) and 7,7a-dihydro-7a-methyl-1-(4-methylphenylsulfonyloxy)-6-phenylselenoindan-5 (6*H*)-one (178 mg, 60%) as a crystalline solid, mp 148–148.5° (from light petroleum-dichloromethane); IR (KBr) 1660 cm⁻¹; δ (CDCl₃) 1.15 (3 H, s), 1.78 (1 H, t, *J* = 14 Hz), 1.98–2.24 (3 H, m), 2.25–2.53 (4 H, m) 2.62–2.80 (1 H, m), 4.18 (1 H, dd, *J*_{6,7} = 6.8 and 5.5 Hz), 4.28 (1 H, dd, *J*_{1,2} = 7.3 and 5.1 Hz), 5.83 (1 H, t, *J* = 1.7 Hz), 7.25–7.4 (5 H, m, aromatics), 7.52 (2 H, d, *J*_A = 8.5 Hz), and 7.73 (2 H, d, *J*_B = 8.5 Hz); *m/z* 476 (M⁺), 330, 314, 312, 258, 223, 184, 155, 148, 147, and 121. Anal. Calcd for C₂₃H₂₄O₄S₂Se : C, 58.1; H, 5.0; S, 6.7. Found: C, 57.7; H, 5.0; S, 6.8.

6.1.1.5.1. (a) Oxidation with Hydrogen Peroxide

The selenide (170 mg, 0.36 mmol) was dissolved in THF (10 mL), the solution was cooled in an ice bath to 0°, and pyridine (57 mg, 100 μL, 0.72 mmol) was added. Hydrogen peroxide (15%; 0.81 mL, 3.6 mmol) was added dropwise during 3 minutes maintaining the temperature below 2°. The solution was allowed to warm to 10° after 1 hour and then to room temperature during 3 hours. The reaction mixture was poured into water (150 mL) and extracted with dichloromethane (3 × 50 mL). The organic phase was washed with saturated sodium carbonate (2 × 25 mL), water (2 × 25 mL), and dried (sodium sulfate). The solvent was removed under reduced pressure to leave a pale yellow oil which was subjected to column chromatography (silica, ether-light petroleum) to give **114** (87 mg, 76%) as a crystalline solid, mp 67–71° (from dichloromethane-light petroleum). IR 2990 m, 2970 m, 1655s, 1635s, 1595s cm⁻¹; ¹H NMR δ (CDCl₃) 1.28 (3 H, s), 2.00–2.28 (2 H, m), 2.32–2.52 (4 H, m), 2.78–2.97 (1 H, m), 4.50 (3 H, t, *J* = 12 Hz), 6.07 (1 H, m), 6.14 (1 H, d *J*_{6,7} = 12 Hz), 6.85 (1 H, d, *J*_{7,6} = 12 Hz), 7.39 (2 H, d, *J*_A = 8.5 Hz), 7.81 (2 H, d, *J*_B = 8.5 Hz); *m/z* 318 (M⁺) 300, 163, 155, 146, 145, 135, 121, 91. Anal. Calculated for C₁₇H₁₈O₄S : C, 64.2; H, 5.7; S, 10.0. Found: C, 63.9; H, 6.0; S, 9.9.

6.1.1.5.2. (b) Oxidation with Chloramine-T

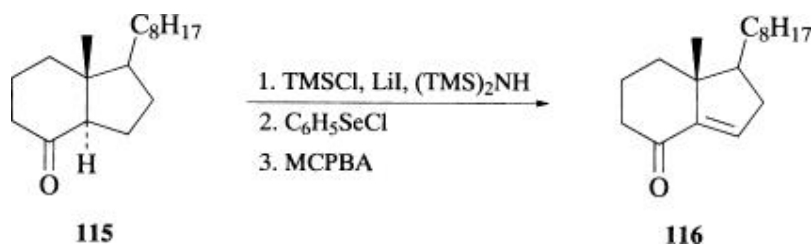
The selenide (212 mg, 0.46 mmol) was dissolved in dichloromethane (25 mL) and placed in a flask containing Chloramine-T (138 mg, 0.49 mmol) and benzyltriethylammonium chloride (20 mg) dissolved in water (25 mL). The solution was stirred until no starting material could be detected by TLC (ca. 15 minutes). The organic layer was separated, washed with water (25 mL), and dried (sodium sulfate), and the solvent removed under reduced pressure to give a white solid which was subjected to column chromatography (silica, light petroleum-dichloromethane-ether) to give dienone **114** as a crystalline solid (134 mg, 95%), identical with that described in section (a).



6.1.1.6. Cycloheptenone [Selenenylation of a Ketone Enolate (Method A-1), Oxidation with Ozone, Pyrolysis of the Selenoxide with Diisopropylamine] (2, 350)

To a cold (-72°) solution of 230 mmol of lithium diisopropylamide in 200 mL of hexane and 1100 mL of THF was added, dropwise with stirring and cooling during 2 hours, a solution of 20.0 g (177 mmol) of cycloheptanone in 20 mL of THF. After the solution had been stirred for 2 hours at -72° , a solution of 33.0 g (177 mmol) of benzeneselenenyl chloride in 50 mL of THF was added, and the resulting solution was stirred and allowed to warm to 0° during a period of 1.5 hours. The resulting mixture was partitioned between aqueous 0.5 M HCl and pentane. After the pentane solution had been washed with aqueous sodium bicarbonate and with brine, it was dried and concentrated. The crude liquid product (38.5 g) contained (TLC, silica gel coating with an diethyl ether-hexane eluent, 1:1, v/v) the keto selenide (R_f 0.56) and some excess diphenyl diselenide (R_f 0.92) but no starting cycloheptanone (R_f 0.76). The crude product was chromatographed on silica gel with diethyl etherhexane eluent (1:9, v/v) to separate 36.8 g (77%) of the liquid keto selenide; n_D^{25} 1.4718; IR (CCl₄) 1705 cm⁻¹ (C = O); ¹H NMR (CCl₄) δ 7.0–7.5 (5 H, m, aryl CH), 3.4–3.8 (1 H, m, COCHSeAr), 0.8–3.0 (10 H, m, aliphatic CH).

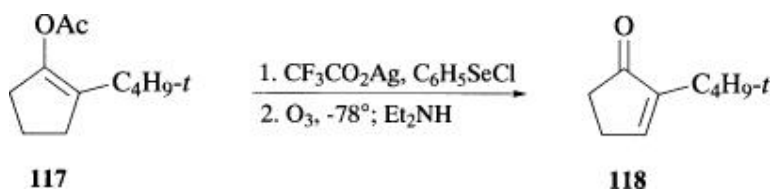
A stream of O₃ and O₂ was passed through a cold (-78°) solution of 20.0 g (75 mmol) of the keto selenide in 100 mL of dichloromethane. When unchanged O₃ appeared in the exit gases, the addition of O₃ was stopped and the solution was purged with a stream of N₂. The solution was treated with 11.8 mL (84 mmol) of diisopropylamine, and the solution was transferred into a boiling solution of 5.9 mL (42 mmol) of diisopropylamine in 400 mL of CCl₄. The resulting solution was allowed to cool to 25° and then washed with aqueous 10% HCl, with aqueous sodium bicarbonate, with brine, and dried. Fractional distillation afforded 7.45 g (90%) of the enone: bp 52–54° (2.0 mm); n_D^{25} 1.4881; IR (CCl₄) 1690 cm⁻¹ (conjugated C = O); UV max (95% ethanol) 225 nm (ϵ 12400), 328 (29).



6.1.1.7. *De-A,B-cholest-14-en-8-one (116) [Preparation and Selenenylation of a Thermodynamic Enol Silyl Ether (Method A-3), Oxidation with *m*-Chloroperoxybenzoic Acid] (250)*

To a dry, 100-mL round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was added ketone **115** (8.77 g, 33 mmol), hexamethyldisilazane (5.8 g, 7.5 mL, 36 mmol), LiI (4.8 g, 36 mmol), TMSCl (3.9 g, 4.6 mL, 36 mmol), and dry dichloromethane (30 mL). The flask was covered (to keep out light) and vigorously stirred at room temperature under nitrogen for 18 hours. To this light brown solution was added dry triethylamine (5 mL), and the resulting mixture was poured into a beaker containing a stirred ice-cold 7% solution of aqueous sodium bicarbonate (100 mL) and ether (50 mL). Separation of the organic layer followed by a brine wash (25 mL), and drying over potassium carbonate gave an orange solution. Concentration yielded a dark orange oil, which upon distillation (Kugelrohr, 0.25 mm, 140°) yielded 10.6 g (96% yield) of the silyl enol ether *de-A,B-8-(trimethylsiloxy)cholest-8(14)-ene* as a light yellow liquid.

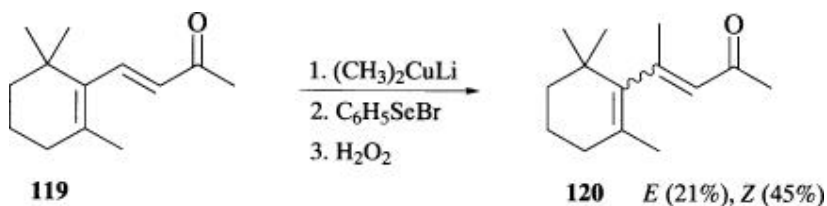
To a dry, 25-mL flask containing dry THF (10 mL) was added the silyl enol ether (2.3 g, 6.8 mmol) and dry pyridine (0.6 mL, 7.5 mmol). The reaction mixture was cooled to -78° and benzeneselenenyl chloride (1.4 g, 7.5 mmol) in THF (4 mL) was added via cannula. After stirring at -78° for 10 minutes, the reaction mixture was poured into 15 mL of acidic (HCl) brine and extracted with dichloromethane. After drying over sodium sulfate, the organic layer was concentrated to yield a yellow oil. The crude selenide (dichloromethane, 50 mL, 0°) was normally directly oxidized with MCPBA (85% titer, 3.2 g, 16 mmol; added in 1 portion). After stirring at 0° for 5 minutes, the cooled mixture was poured into basic (NaOH) brine, the layers were separated, and the aqueous layer was extracted with dichloromethane (10 mL). The combined organic extracts were washed with acidic (HCl) brine, dried over sodium sulfate, and concentrated to give a dark oil. Purification of the crude oil by flash chromatography (5% ethyl acetate-petroleum ether) gave the enone **116** (1.3 g, 71% yield) as a light yellow oil.



6.1.1.8. 2-*tert*-Butylcyclopent-2-enone (**118**) [Reaction of an Enol Acetate with Silver Trifluoroacetate and Benzeneselenenyl Chloride (Method A-3), Oxidation with Ozone, Pyrolysis with Diethylamine] (**351**)

To a solution of silver trifluoroacetate (14.4 g; 63 mmol) in benzene (280 mL) was added at room temperature under N₂ a solution of 1-acetoxy-2-*tert*-butylcyclopentene (**117**) (10.4 g; 57 mmol) in benzene (28 mL) followed by benzeneselenenyl chloride (12.4 g; 63 mmol). After stirring for 1 minute, brine (2.3 mL) was added along with Na₂CO₃ (2.35 g) in water (2.3 mL). After filtering through Celite, drying (magnesium sulfate) and solvent removal, chromatography (benzene-hexane, 2:8) of the residue gave 2-*tert*-butyl-2-phenylselenocyclopentanone, (13.7 g, 82%). R_f (benzene:hexane) 3:7, 0.20; IR 1727, 1602 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 7.7–7.1 (m, 5 H, phenyl), 2.5–1.6 (m, 6 H), 1.14 (s, 9 H, *t*-Bu).

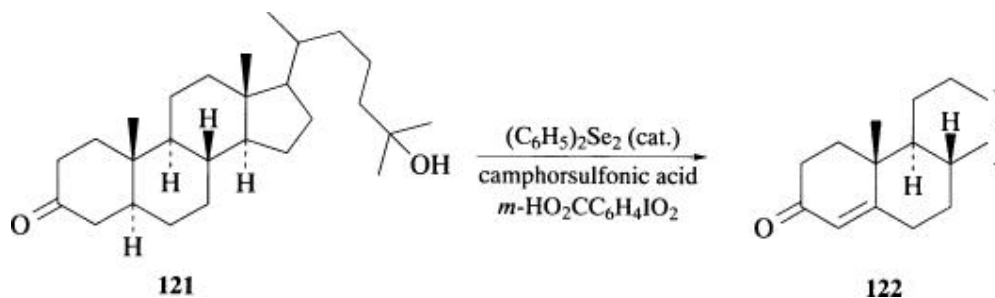
A solution of the selenide (5.1 g; 17.3 mmol) in dichloromethane (150 mL) was cooled to –78° and treated with O₃ until a persistent green color was seen. After flushing with N₂, diethylamine (3.6 mL; 34.6 mmol) was added and the mixture was warmed to 40°. The solution was successively washed with 20% HCl and a saturated sodium bicarbonate solution. Usual workup by chromatography (benzenehexane, 1:1) and distillation yielded **118** (1.76 g; 74%); bp_{12 mm} 76°; R_f (benzene-hexane, 1:1) 0.20; IR 1700–1620 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 7.22 (t, 1 H, C₃), 2.60–2.28 (m, 4 H, C_{4,5}), 1.17 (s, 9 H, *t*-Bu); mass spectrum, m/z (rel intensity, EI, 70 eV): 138 (M, 73), 123 (86), 96 (58), 95 (82), 41 (100).



6.1.1.9. 4-(2',6',6'-Trimethyl-1 ϕ -cyclohexen-1'-yl)-3-penten-2-one (**120**)

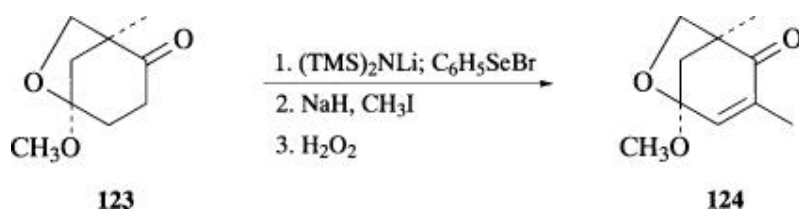
[Selenenylation of a Ketone Enolate Prepared by Cuprate Conjugate Addition (Method A-11), Oxidation with Hydrogen Peroxide] (352)

To a suspension of Cu_2I_2 (15.6 g, 81.9 mmol) in ether (600 mL), a 1.6 M solution of methyllithium in ether (100 mL, 160 mmol) was added at -40° , and the mixture was stirred for 20 minutes. β -Ionone (**119**, 12.8 g, 66.6 mmol) in ether (100 mL) was added slowly at -40° , and the mixture was allowed to warm to -10° over 20 minutes. Again at -40° , a solution of benzeneselenenyl bromide in THF (120 mL) [prepared by reaction of diphenyl diselenide (25.7 g, 82.3 mmol) and Br_2 (2.92 mL, 57.0 mmol) in THF at 0°] was added rapidly. The cooling bath was removed, and the mixture was allowed to warm to room temperature, poured into ether-pentane 1:1 (1 L) and aq. ammonium chloride (satd.; 500 mL) and worked up. The crude product was dissolved in pyridine (20 mL) and dichloromethane (500 mL), and hydrogen peroxide (15%; 882 mmol) was added dropwise at room temperature (highly exothermic reaction). After 1 hour at room temperature, aq. sodium bicarbonate (10%; 125 mL) was added, the organic phase was washed with 1 M aq. HCl and worked up. Column chromatography [silica, acetone-dichloromethane-hexane (1:100:100)] of the residue yielded (*E*)-**120** (2.94 g, 21%), (*Z*)-**120** (6.24 g, 45%), saturated methyl addition product (0.39 g, 3%), and 1,2-methyl addition product (0.55 g, 4%). *E*-**120**: bp $60^\circ/0.01$ torr. UV (0.0591 mg in 5 mL): 233 (13800). UV (4.8 mg in 5 mL): 331 (43), end absorption to 400. IR 2960s, 2925s, 2905s (sh). ^1H NMR δ 0.98 (s, $2\text{CH}_3\text{-C}(6\phi)$); 1.34–2.10 (m, 6 H); 1.48 (s, $\text{CH}_3\text{-C}(2\phi)$); 2.09 (s, 3 H-C(1)); 2.12 (d, $J = 1.5$ Hz, 3 H-C(5)); 5.78 (m, $w_{1/2} = 3$ Hz, H-C(3)); ^{13}C NMR (62°) δ 20.8, 29.0, 31.8 (4q, 2q at 29.0 4CH_3); 22.5 (q, C(5)); 19.3 (t, C(4')); 31.6 (t, C(3')); 39.7 (t, C(5')); 126.7 (d, C(3)); 34.3 (s, C(6')); 126.3, 143.4 (2s, C(1'), C(2 ϕ)); 157.5 (s, C(4)); 198.2 (s, C(2)); mass spectrum, m/z (rel intensity) 206 (14, M^+ , $\text{C}_{14}\text{H}_{22}\text{O}$), 192 (15), 191 (100), 163 (9), 149 (19), 137 (15), 136 (15), 135 (12), 123 (25), 107 (14), 95 (14), 91 (12), 43 (39), 41 (12). Anal. calc. for $\text{C}_{14}\text{H}_{22}\text{O}$ (206.32): C 81.50, H 10.75; found: C 81.31, H 10.91.



6.1.1.10. 25-Hydroxycholest-4-en-3-one (**122**) [Oxidation of a Ketone with Catalytic Diphenyl Diselenide, Acid Catalyzed, Using Iodylbenzoic Acid as Reoxidant (Method B-2) (**231**)]

A mixture of diphenyl diselenide (16 mg, 0.10 mmol), camphorsulfonic acid (120 mg, 0.49 mmol), and *m*-iodylbenzoic acid (290 mg, 0.98 mmol) in THF (1 mL) was refluxed for 15 minutes. A solution of keto alcohol **121** (197 mg, 0.98 mmol) in THF (3 mL) was added and the mixture was refluxed for another 30 minutes. After having cooled to room temperature, the mixture was poured into saturated aqueous sodium bicarbonate (10 mL) and extracted with ether (3 × 10 mL). Usual workup afforded a crude residue, which was purified by preparative layer chromatography (hexane-ether, 4:6). The major product was the enone **122** (135 mg, 69%), mp 148–150° (from CH₃OH); [α]_D + 86.7° (c 0.475); IR (CHCl₃) 1660, 1620 cm⁻¹; ¹H NMR δ(400 MHz, CDCl₃, partial) 0.71 (3 H, s), 0.93 (3 H, d, *J* = 6 Hz), 1.18 (3 H, s), 1.21 (6 H, s), and 5.73 (1 H, s); mass spectrum *m/z* 385 (46), 382 (M⁺ – 18, 100), 367 (45), 340 (43), 298 (46), 297 (46), 269 (38), 229 (20), and 124 (27%).



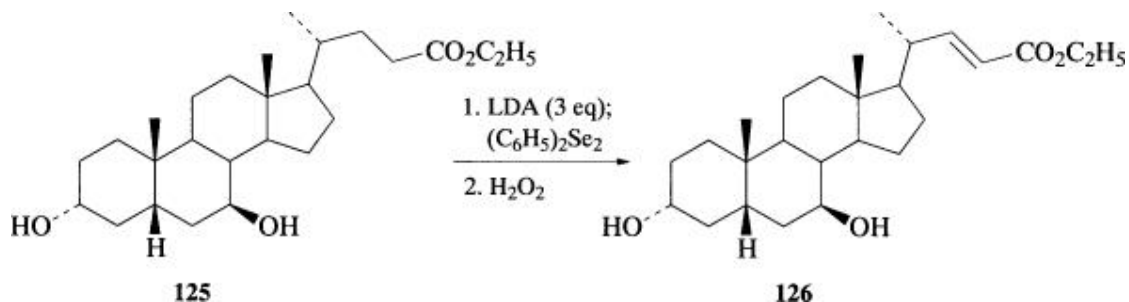
6.1.1.11. 5-Methoxy-1,3-dimethyl-6-oxabicyclo[3.2.1]oct-3-en-2-one (**124**) [Alkylation of an α-Phenylseleno Ketone (Method D-1)] (**353**)

To a (TMS)₂NLi solution prepared from (TMS)₂NH (1.5 mL) and *n*-butyllithium (1.49 N, 4.7 mL, 7.0 mmole) in dry THF (8 mL) was added dropwise a solution of ketone **123** (1.0 g, 5.9 mmol) in dry THF (8 mL) at –78°. After stirring for 1 hour at –78°, benzeneselenenyl bromide (1.8 g, 7.6 mmol) in dry THF (8 mL) was added dropwise. After stirring for 20 minutes, the reaction mixture was poured into water and extracted with ether. The extract was washed with water, saturated sodium bicarbonate solution, and brine, dried (magnesium sulfate), and concentrated in vacuo. The residue was roughly chromatographed over silica. Elution with *n*-hexane-ethyl acetate (25:1 ~ 20:1) gave the unstable phenylseleno ketone. IR (film) 3050 (w), 2970 (s), 2930 (s), 1690 (s) cm⁻¹. This was employed for the next step without further purification.

To a stirred suspension of NaH (0.74 g, 18.5 mmol) in dry THF (10 mL) was added the phenylseleno ketone (ca. 5.9 mmol) in dry THF (10 mL) at 0°. To this solution, CH₃I (2 mL, 32.1 mmol) was added. After stirring for 5 hours at 0°, the reaction mixture was poured into saturated ammonium chloride solution, and extracted with ether. The extract was washed with water, saturated

sodium bicarbonate solution, and brine, dried (magnesium sulfate), and concentrated in vacuo. The residue was chromatographed over silica (60 g). Elution with hexane-ethyl acetate (25:1 to 20:1) gave 1.85 g (93%) of unstable (1*R*, 3*RS*, 5*S*)-5-methoxy-1,3-dimethyl-3-phenylseleno-6-oxabicyclo[3.2.1]octan-2-one, IR (film) 3060 (w), 2980 (s), 2940 (s), 1695 (s) cm⁻¹. This was employed for the next step without further purification.

To a solution of the alkylated phenylseleno ketone (1.85 g, 5.46 mmol) and solid sodium bicarbonate (1 g) in dry THF (20 mL) was added 35% hydrogen peroxide (1 mL) at 20°. After stirring for 1 hour at room temperature, the reaction mixture was quenched with water and extracted with ether. The extract was washed with saturated Na₂S₂O₃ solution, saturated sodium bicarbonate solution, and brine, dried (potassium carbonate), and concentrated in vacuo. The residue was chromatographed over alumina (grade IV, 30 g). Elution with *n*-hexane-ethyl acetate (40:1 to 30:1) gave 0.65 g (65%) of **124**, n_D^{17} 1.4831; $[\alpha]_D^{17} - 79.8^\circ$ (c 1.75, methanol); IR (film) 2900(s), 2950(s), 1680(s) cm⁻¹; NMR (100 MHz, C₆D₆) δ 1.12 (3 H, s), 1.47 (1 H, d, $J = 10$ Hz), 1.72 (3 H, d, $J = 2$ Hz), 1.80 (1 H, dd, $J = 10$ and 3 Hz), 3.26 (3 H, s), 3.35 (1 H, d, $J = 8$ Hz), 3.43 (1 H, d, $J = 8$ Hz), 6.76 (1 H, dt, $J = 3$ and 2 Hz). Mass spectrum, *m/z*, found: 182.0923; calcd for C₁₀H₁₄O₃: 182.0943.



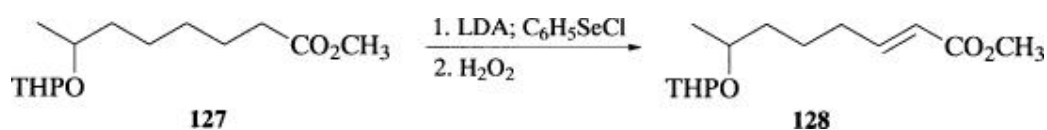
6.1.1.12. (*E*)-Ethyl 3 α , 7 β -Dihydroxy-5 β -chol-22-en-24-oate (**126**).

[Selenenylation of an Ester Dihydroxy Enolate with Diphenyl Diselenide (Method A-1), Oxidation with Hydrogen Peroxide] (354)

A solution of ester **125** (12 g, 28.5 mmol) in THF (80 mL) was added dropwise to a solution of lithium diisopropylamide [from addition of *n*-butyllithium in hexane (95 mL of a 1.35 M solution) to a solution of diisopropylamine (14.3 g) in THF (150 mL)] kept under nitrogen at -78°. After the mixture was stirred for 15 minutes, a solution of diphenyl diselenide (17.8 g, 57 mmol) in THF (70 mL) was added dropwise to the solution of the enolate, and the resulting solution was stirred at -78° for 2 hours; the reaction mixture was allowed to warm to

room temperature, poured onto a 10% ammonium chloride solution (500 mL), and then extracted with ethyl acetate (5 × 50 mL). The combined organic phases were washed with 1.6 N HCl (3 × 30 mL) and with saturated aqueous sodium bicarbonate solution (3 × 30 mL). The organic phase was dried (magnesium sulfate) and concentrated in vacuo. Chromatography of the oily residue (30 g) on silica gel column and elution with chloroform-methanol, 99:1, gave 13.86 g (84%) of the 23-phenylseleno derivative: mp 63–65°; IR (CHCl₃) 3610, 3450 (OH), 1725 (CO) cm⁻¹; mixture of isomers ¹H NMR (CDCl₃) δ 0.63 and 0.70 (3 H, ss, 18 Me), 0.97 (6 H, s, 19 and 21-Me), 1.16 (3 H, t, *J* = 7 Hz, OCH₂CH₃), 3.33–3.88 (2 H, m, CHOH), 4.05 (2 H, dq, *J* = 7 Hz, OCH₂CH₃), 7.10–7.64 (5 H, brm, aromatic H's). Anal. (C₂₆H₄₈O₄Se) C, H.

A solution of 36% hydrogen peroxide (1.5 mL) was added dropwise to a stirred solution of the selenide (1.2 g, 2.09 mmol) in dichloromethane (30 mL) at room temperature. After 15 minutes, the reaction mixture was washed with water (2 × 10 mL), filtered by passing over silica gel-Celite (5 g, 1:1, w/w), dried (magnesium sulfate), and concentrated in vacuo. Flash chromatography of the residue over silica gel and elution with chloroform-methanol, 99:1, afforded *E* olefin **126** (0.86 g, 99%): mp 78–81°; IR 3600, 3420 (OH), 1705 (CO), 1650 (C=C) cm⁻¹; ¹H NMR (CDCl₃) δ 0.72 (3 H, s, 18-Me), 0.97 (3 H, s, 19-Me), 1.27 (3 H, t, *J* = 7 Hz, OCH₂CH₃), 2.40 (2 H, m, OH) 3.53 (2 H, m, CHOH), 4.13 (2 H, q, *J* = 7 Hz, OCH₂CH₃), 5.67 (1 H, d, *J* = 16 Hz, 23-CH), 6.73 (1 H, dd, *J*₂₀₋₂₂ = 9.5 Hz and *J*₂₂₋₂₃ = 16 Hz, 22-CH). Anal. (C₂₆H₄₂O₄) C, H, O.



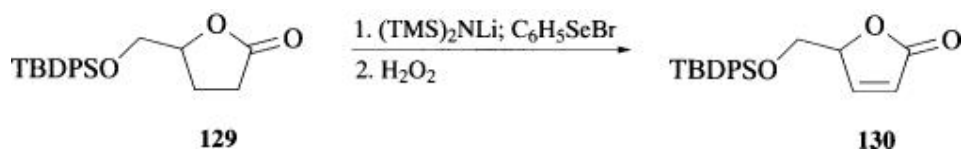
6.1.1.13. (±)-Methyl 7-(Tetrahydropyranyloxy)oct-2-enoate (**128**)

[Selenenylation of an Ester Enolate with Benzeneselenenyl Bromide (Method A-1), Oxidation with Hydrogen Peroxide] (355)

n-Butyllithium (2.3 mL of 2.5 M, 5.7 mmol) was added via syringe to a solution of diisopropylamine (581 mg, 5.7 mmol) in THF (20 mL) at -78° and under an atmosphere of argon. After stirring for 10 minutes, a solution of **127** (1.14 g, 4.4 mmol) in THF (10 mL) was added. After another 20 minutes, benzeneselenenyl bromide (1.4 g, 5.7 mmol) in THF (10 mL) was added. Stirring was continued for 1 hour and saturated aqueous ammonium chloride solution was added. The resulting mixture was extracted with ether and the extracts were dried, filtered, and concentrated to dryness.

The crude oil (2.1 g) was dissolved in dichloromethane (40 mL) and cooled to 0°. A solution of 30% aqueous hydrogen peroxide (20 mL) was added slowly

over 40 minutes. After being stirred for another hour at room temperature, saturated aqueous sodium bicarbonate was added. The mixture was extracted with dichloromethane and the organic extracts were washed with brine solution, dried, filtered, and concentrated to give a yellow oil. Flash chromatography of the crude oil and elution of the column with 10% ethyl acetate in hexane gave 701 mg (62%) of pure **128** as an oil: IR 2930, 2860, 1718, 1650 cm^{-1} ; $^1\text{H NMR}$ δ 1.10, 1.22 (both d, $J = 6.0$ Hz each, total 3 H), 1.40–2.00 (m, 10 H), 2.22 (m, 2 H), 3.74 (s, 3 H), 3.40–4.10 (m, 3 H), 4.70 (m, 1 H), 5.87 (d, $J = 15$ Hz, 1 H), 7.07 (dt, $J = 15$ Hz, $J_{\text{H}} = 8.0$ Hz, 1 H); mass spectrum, m/z 256, 225, 199, 171, 143, 98, 87, 74, 69, 55 (base); $M^+ - 1$ 255.1594 (calcd for $\text{C}_{14}\text{H}_{23}\text{O}_4$ 255.1596).

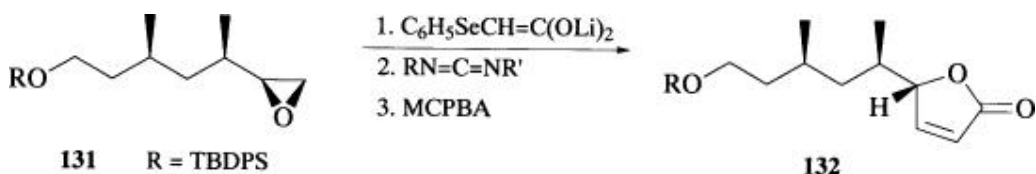


6.1.1.14. (4*S*)-4-(*tert*-Butyldiphenylsiloxy)methyl-2-buten-4-olide (**130**).
 [Selenenylation of a Lactone Enolate with Benzeneselenenyl Bromide,
 Oxidation with Hydrogen Peroxide] (168)

Lactone **129** (17.7 g, 50 mmol) in THF (75 mL) was added dropwise to a THF solution (200 mL) containing lithium hexamethyldisilazide (prepared from bis(trimethylsilylamine), 11.6 mL, 1.1 equiv, and *n*-butyllithium, 31.2 mL of a 1.6 M solution in hexane, 1.0 equiv.) at -78° over 5 minutes. After 25 minutes the enolate was quenched by the addition of benzeneselenenyl bromide (11.7 g, 1.0 equiv.) in THF (50 mL) and immediately afterward with 1 N HCl (200 mL). The reaction was poured into ether (500 mL) and the ethereal layer worked up in the usual manner to afford a crude mixture of epimeric monoselenides. Chromatography (1:10 ethyl acetate-hexane) provided the two monoselenides as yellow oils (23.58 g, 95%), for the less polar isomer (78%); $[\alpha]_{\text{D}} + 17.63^\circ$ (c 2.2 CHCl_3); more polar isomer (22%); $[\alpha]_{\text{D}} + 43.3^\circ$ (c 2.12, CHCl_3).

This mixture of selenides (13.1 g, 25.7 mmol) in dichloromethane (200 mL) was added dropwise to a vigorously stirred solution of ice-cold 30% hydrogen peroxide (20 mL) over 40 minutes. The heterogeneous reaction was stirred for a further 15 minutes and the organic phase was then washed with water (4×100 mL), saturated brine (1×100 mL), dried (magnesium sulfate), and evaporated to an oil. Chromatography (20% ethyl acetate in hexane) gave the butenolide **130** as a white crystalline solid (8.85 g, 97%), mp $83\text{--}84^\circ$; $[\alpha]_{\text{D}} - 85.2^\circ$ (c 1.2, CHCl_3). On larger runs, the yield varied between 72 and 90%. IR (film) 1700 cm^{-1} (C = O); mass spectrum found m/z 295.0787 ($M-t\text{-Bu}$); $^1\text{H NMR}$; 7.65–7.61 (4 H, m); 7.47–7.37 (7 H, m); 6.17 (1 H, dd, $J = 5.7$,

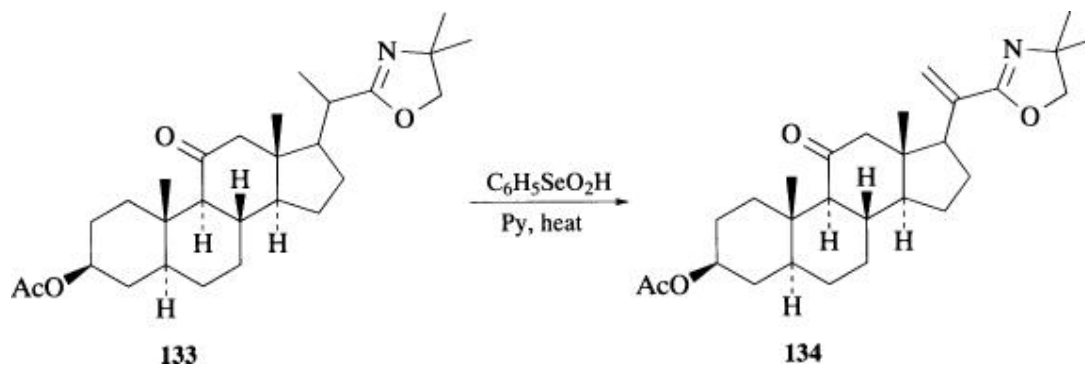
2.0 Hz); 5.08–5.05 (1 H, m); 3.90 (1 H, dd, $J = 10.9, 4.4$ Hz); 3.87 (1 H, dd, $J = 10.9, 4.9$ Hz); 1.04 (9 H, s).



6.1.1.15. Lactone **132** [Alkylation of Dilithio(phenylseleno)acetic Acid with an Epoxide (Method D-1), Oxidation with Hydrogen Peroxide] (168)

To a solution of hexamethyldisilazane (70.2 μL , 0.333 mmol) in THF (5 mL) at 0° was added *n*-butyllithium (208 μL of a 1.6 M solution, 1.0 equiv.) and the base was allowed to form for 20 minutes. This was treated with phenylselenoacetic acid (35.8 mg, 0.167 mmol, 0.5 equiv.) in THF (500 mL) and the dianion allowed to form at room temperature for 1 hour. Epoxide **131** (35.8 mg, 0.0833 mmol, 0.25 equiv.) was added in THF (1 mL) and the mixture stirred at room temperature for 15 hours. The resulting yellow solution was partitioned between ether (35 mL) and 2 M HCl (2 mL), the ethereal layer washed with water (2×5 mL) and saturated brine (10 mL), dried (magnesium sulfate) and evaporated to a yellow oil. The crude hydroxy acid was immediately redissolved in dichloromethane (10 mL) and treated with ethyl 3-(*N,N*-dimethylamino)propyl carbodiimide (31.9 mg, 2.0 equiv.) and 4-dimethylamino-pyridine (~5 mg, catalytic) at room temperature for 30 minutes. The mixture was poured into ether (50 mL) and water (50 mL), given a standard workup and evaporated to give the crude epimeric mixture of α -phenylselenolactones which were oxidized directly.

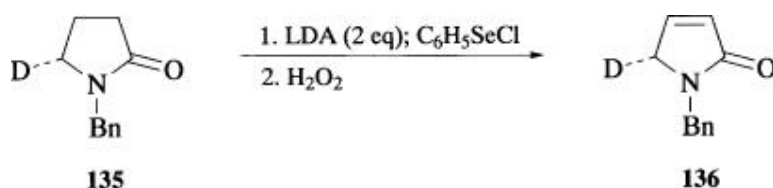
The mixture of epimeric selenides in dichloromethane (20 mL) was added dropwise to an ice-cold solution of 30% hydrogen peroxide (5 mL) with vigorous stirring. After the addition was complete, stirring was continued at room temperature for 45 minutes, after which the organic layer was separated and washed several times with water (3×20 mL), dried (magnesium sulfate), and evaporated to a crude oil. Column chromatography (5–10% ethyl acetate in hexane) afforded the lactone **132** as a colorless oil (29 mg, 69%; ^1H NMR δ 7.69–7.64 (4 H, m); 7.45–7.37 (7 H, m); 6.6 (1 H, bds); 4.93–4.90 (1 H, m); 3.77–3.63 (2 H, m); 1.98–1.89 (1 H, m); 1.80–1.70 (1 H, m); 1.70–1.60 (1 H, m); 1.38 (1 H, ddd, $J = 14.0, 8.0, 5.5$ Hz); 1.28–1.18 (1 H, m); 1.14–1.06 (1 H, m); 1.04 (9 H, s); 0.87 (3 H, d, $J = 6.8$ Hz); 0.84 (3 H, d, $J = 6.7$ Hz).



6.1.1.16. 2-(3 β -Acetoxy-11-oxo-5

α -pregn-20-yl)-4,4-dimethyl-4,5-dihydrooxazole (**133**) [Oxidation of a Dihydrooxazole with Benzeneseleninic Acid (Method B-2)] (90)

A mixture of the dihydrooxazole **133** (162 mg), benzeneseleninic acid (90 mg), and pyridine (1 mL) in dry benzene (10 mL) was heated to reflux under nitrogen for 6 hours with azeotropic removal of water. The solvents were removed under reduced pressure and the residue chromatographed on silica (ethyl acetate-hexane, 1:2) to give the pure α , β -unsaturated dihydrooxazole **134** (131 mg, 81%), m.p. 144–145° (methanol); $[\alpha]_D = +6^\circ$ (c 1.2); IR (dichloromethane) 1735, 1700, 1645, 1600 cm^{-1} ; $^1\text{H NMR}$ δ 6.20 (1 H, s), 5.56 (1 H, s), 4.78 (1 H, br), 4.03 (2 H, s), 1.32 and 1.29 (6 H, 2 \times s), and 1.04 and 0.50 (6 H, 2 \times s). Anal. Calc. for $\text{C}_{28}\text{H}_{41}\text{NO}_4$: C, 73.80; H, 9.07; N, 3.07. Found: C, 73.25; H, 9.2; N, 3.3.

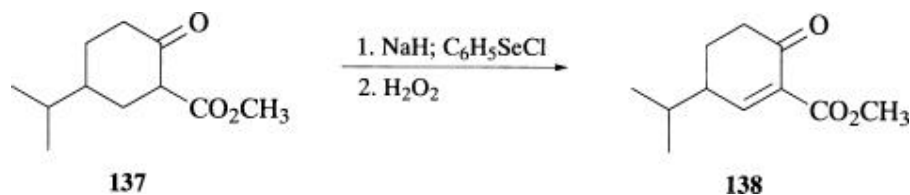


6.1.1.17. (5R)-[5-D]-1-Benzyl-3-pyrrol-2(5H)-one (**136**). [Selenenylation of a γ -Lactam Enolate Using Two Equivalents of Base (Method A-1), Oxidation with Hydrogen Peroxide] (356)

A solution of butyllithium in hexane (8 mL, 13.66 mmol) and diisopropylamine (freshly distilled, 1.94 mL, 13.66 mmol) in dry THF (14 mL) was stirred at 0° under argon. After cooling to -78° , compound **135** (1.2 g, 6.83 mmol) in dry THF (7 mL) was added. After 10 minutes benzeneselenenyl chloride (1.3 g, 6.83 mmol, recrystallized from hexane) in dry THF (8 mL) was slowly added. After 5 minutes, the reaction was allowed to warm to room temperature and then poured into formate buffer (pH 3; 180 mL) and extracted with ether. The

extract was dried and evaporated, and the oily residue (2.35 g) was purified by flash chromatography (hexane-ethyl acetate 1.90–2.60 (2 H, m, CH₂), 2.95 (1 H, m, CHD), 3.98 (1 H, m, CHSePh), 4.42 (2 H, s, CH₂ benzylic), and 7.00–7.85 (10 H, aromatic complex); m/z: 331, 175, 157, 91 (100%). A sample was distilled for analytical purposes to afford pure selenide, bp 240° (0.2 mm Hg). Anal. Calcd for C₁₇H₁₆DNOSe : C, 61.6; H, 5.5; N, 4.2. Found: C, 61.5; H + D 5.4; N, 4.1.

The phenylselenopyrrolidinone (782 mg, 2.36 mmol) was dissolved in ethanol (8.6 mL) and the solution was cooled to 0°. Hydrogen peroxide (35%, 1.4 mL) was then added dropwise and the mixture was stirred at 0° (the reaction was monitored by TLC, dichloromethane-acetone, 85:15). After 30 minutes, a solution of ferrous sulfate heptahydrate (4.12 g, 14.8 mmol) in water (20 mL) was added slowly. The mixture was diluted with water (40 mL), and extracted with dichloromethane. The organic layer was washed with aqueous sodium bicarbonate and water, dried, and evaporated. The pyrrolone **136** (344 mg, 1.98 mmol), 83.7% yield was obtained after purification by flash chromatography (eluant dichloromethane-acetone 87: 13); IR 3000, 2150, 1675br cm⁻¹; ¹H NMR δ3.85 (1 H, m, CDH), 4.61 (2 H, s, CH₂ benzylic), 6.20 (1 H, d, CH = , J = 6 Hz), 7.02 (1 H, d, CH = , J = 6 Hz), and 7.26 (5 H, aromatic complex); [α]_D = + 1.48° (c 5.19, CHCl₃); m/z: 174 (M⁺), 173, 106, and 91 (100%). A sample crystallized from diisopropyl ether had mp 60–61°. Anal. Calcd for C₁₁H₁₀DNO : C, 75.8, H + D, 6.9; N, 8.0. Found: C, 75.6; H + D, 6.8; N, 7.9.



6.1.1.18. 2-(Methoxycarbonyl)-4-isopropylcyclohex-2-en-1-one (138)
[Selenenylation of a β-Keto Ester Enolate (Method A-1), Oxidation with Hydrogen Peroxide] (357)

β-Keto ester **137** (22.0 g, 111 mmol) was added dropwise to a stirred, cooled (0°) suspension of hexane-washed NaH (6.65 g of a 60% dispersion, 166 mmol) in THF (400 mL). The mixture was then warmed to room temperature over 1 hour and then cooled to 0°. A solution of benzeneselenenyl chloride (25.5 g, 133 mmol) in THF (75 mL) was added in one portion. The reaction was warmed to room temperature and quenched with saturated aqueous sodium bicarbonate (400 mL). Extractive workup (ethyl acetate) and flash chromatography (silica, 10% hexane-ethyl acetate) gave 36.5 g (93%) of

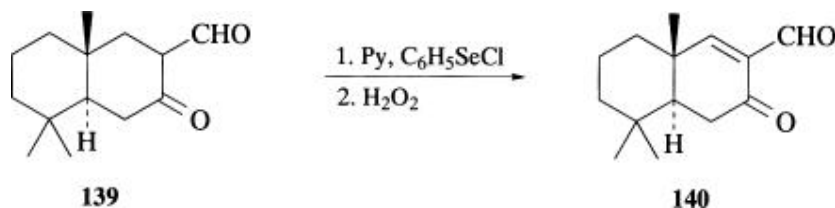
selenide (thick oil) as a mixture of *cis* and *trans* isomers: ^1H NMR (90 MHz, CDCl_3) δ 7.78–7.55 (m, 2 H), 7.45–7.20 (m, 3 H), 3.75 and 3.68 (2 s, integrated ratio = 2:1, 3 H), 2.72–1.24 (m, 8 H), 1.90 (apparent t, 6 H).

To a vigorously stirred solution of selenide (28 g, 79.2 mmol) in dichloromethane (150 mL) was added 5 mL of hydrogen peroxide (30%, 13.5 mL, 119 mmol) in water (30 mL). After 10 minutes, the solution turned yellow and was cooled to 0° , and the remaining hydrogen peroxide was added dropwise. The mixture was stirred until a precipitate formed. Analysis by TLC indicated consumption of the starting material (ca. 20 minutes). Saturated aqueous sodium bicarbonate (200 mL) was added, the mixture was extracted with dichloromethane, and the combined organic layers were successively washed with saturated aqueous sodium bicarbonate and brine. Drying (magnesium sulfate) and concentration provided 15.3 g (98%) of enone **138** (oil) as a 13:1 mixture of keto/enol forms. Attempts to purify the product further (distillation or silica gel chromatography) resulted in increasing enolization: IR (CDCl_3) 2960, 2870, 1740, 1715, 1685, 1280 cm^{-1} ; ^1H NMR (250 MHz, CDCl_3) δ 7.62 (t, 1 H, $J = 2$ Hz), 3.79 (s, 3 H), 2.59 (dt, 1 H, $J = 16, 4$ Hz), 2.49–2.34 (m, 2 H), 2.12–1.72 (m, 3 H), 0.99 (d, 3 H, $J = 3.6$ Hz), 0.97 (d, 3 H, $J = 3.6$ Hz); mass spectrum (EI) for $\text{C}_{11}\text{H}_{16}\text{O}_3$, calcd 196.1099, found 196.1094.

6.1.1.19. 2-Carbomethoxycyclopent-2-enone (Eq. 47). [Selenenylation of a β -Keto Ester with Pyridine-Benzeneselenenyl Chloride (Method A-2), Oxidation with Hydrogen Peroxide] (358)

Benzeneselenenyl chloride (21.6 g, 0.11 mol) was dissolved in dichloromethane (500 mL) cooled to 0° and treated with pyridine (9.9 mL 1.2 equiv.). After 15 minutes 2-carbomethoxycyclopentanone (14.5 g, 0.9 equiv.) was added, and the reaction stirred at 0° for 90 minutes and then allowed to warm to room temperature. The reaction was poured into 10% aqueous HCl (400 mL) and the organic phase was separated and washed with saturated sodium bicarbonate solution (100 mL). Evaporation of the solvent gave 2-carbomethoxy-2-phenylseleno-cyclopentanone as a yellow oil (30.5 g, 100%); IR (film) 3080, 2980, 1750, 1730, 1440, 1225, 1136, 1000 cm^{-1} ; ^1H NMR (60 MHz) δ 7.8–7.0 (5 H, m), 3.75 (3 H, s), and 2.8–1.6 (6 H, m); m/z 298 (M^+), 266.

The selenide (5.0 g, 16.8 mmol) was dissolved in dichloromethane (350 mL) and added dropwise over 0.5 hour, with vigorous stirring, to hydrogen peroxide (ca. 28%, 6.5 mL, 3 equiv.) at 0° . After stirring for a further 0.5 hour at room temperature the reaction was worked up to give enone as an unstable light-brown oil (2.04 g, 96%); IR (film) 2950, 1750, 1720, 1620 cm^{-1} ; δ (60 MHz) 8.40 (1 H, t, $J = 2$ Hz, $\text{CH} = \text{C}(\text{CO}_2\text{Me})\text{CO}$), 3.86 (3 H, s, CO_2Me), 2.95–2.35 (4 H, m, $\text{CH}_2\text{CH}_2\text{CO}$).



6.1.1.20. 3,4,4a α ,5,6,7,8,8a-Octahydro-5,5,8a

β -trimethyl-3-oxonaphthalene-2-carboxaldehyde (**140**) [Selenenylation of a β -Keto Aldehyde with Pyridine-Benzene-selenenyl Chloride (Method A-2), Oxidation with Hydrogen Peroxide] (359)

To an ice-cooled solution of 7.66 g (40 mmol) of benzeneselenenyl chloride in 300 mL of dichloromethane was added 3.48 g (44 mmol) of pyridine and 8.88 g (40 mmol) of **139** in 25 mL of dichloromethane. The reaction mixture was stirred for 1 hour and washed with 25 mL of 4 N HCl and with 50 mL of brine. The dichloromethane solution was cooled in ice, and 4.5 mL of 30% hydrogen peroxide was added in three portions with intervals of 15 minutes. The residue was purified by flash column chromatography on silica gel using 4:1 petroleum ether/ether as eluant to give 8.45 g (96%) of **140** as a colorless oil. $^1\text{H NMR}$ δ 0.97 (s, 3 H), 0.99 (s, 3 H), 1.20 (s, 3 H), 1.3–1.9 (m, 7 H), 2.50 (dd, $J = 5.2, 1.5$ Hz, 2 H), 7.34 (s, 1 H), 10.07 (s, 1 H).

6.1.1.21. Recovery of Diphenyl Diselenide Using Sodium Thiosulfate (2)

The reaction mixture from oxidation of 0.1 mole of a selenide with hydrogen peroxide in dichloromethane was extracted several times with Na_2CO_3 . The aqueous phase was neutralized with concentrated HCl and kept acidic by further additions of acid while 48.2 g (0.306 mol) of sodium thiosulfate was added gradually over 30 minutes. After stirring the solution for 2 hours an additional 7.9 g of sodium thiosulfate was added and the solution was stirred for 18 hours as diphenyl diselenide precipitated. Filtration gave 15.26 g, 89%. Recrystallization from ethanol gave 12.0 g (70%) of pure diphenyl diselenide.

6.1.1.22. Recovery of Diphenyl Diselenide Using Sodium Dithionite (89)

After oxidation was complete, the organic phase was thoroughly extracted with sodium bicarbonate. The combined aqueous extracts were treated at room temperature with a saturated solution of sodium dithionite (excess) for 1 hour. The aqueous phase was then oxidized by a stream of air for 1 hour to destroy excess hydrosulphite, and diphenyl diselenide was recovered by extraction with toluene (yield not reported).

7. Tabular Survey

The tabular survey includes all examples found in the literature to the end of 1990. Searches were conducted by examining all relevant papers in *CA Selects: Selenium and Tellurium Chemistry*, by direct inspection of the literature, and by *Science Citation Searches* using key papers. The last was less effective for more recent examples since fewer and fewer authors cited the key papers which first described the reactions.

Table entries are in order of increasing carbon number of the **product**, and then in order of increasing unsaturation, with frequent departures from the latter criterion to group closely related compounds. The carbon count does not include parts of molecules connected by heteroatoms.

The reagents specified are those reported for conversion of the starting material to the product shown. In most cases, this corresponds to the process identified in the column entitled Method, but in some cases there are functional group manipulations between the introduction of selenium and its oxidative removal. These steps are usually not shown, and the starting material is reported as the selenide. In cases for which a specific selenylation or oxidation procedure is not reported the symbols [RSe] and [Ox] are used.

The following abbreviations are used in the tables:

Ac	acetyl
Bn	benzyl
Bz	benzoyl
Boc	<i>tert</i> -butoxycarbonyl
Diglyme	diethylene glycol dimethyl ether
DMF	<i>N,N</i> -dimethylformamide
Ether	diethyl ether
HMPA	hexamethylphosphoric triamide
LCA	lithium cyclohexylisopropylamide
LDA	lithium diisopropylamide
LTMP	lithium 2,2,6,6-tetramethylpiperidide
MCPBA	<i>m</i> -chloroperoxybenzoic acid
MOM	methoxymethyl
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
PCC	pyridinium chlorochromate

Phth	phthaloyl
Py	pyridine
rt	room temperature
SEM	2-trimethylsilylethoxymethyl
TBDMS	<i>tert</i> -butyldimethylsilyl
TBDPS	<i>tert</i> -butyldiphenylsilyl
THF	tetrahydrofuran
THP	tetrahydropyranyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TMS	trimethylsilyl
Ts	<i>p</i> -toluenesulfonyl

Table I. Methods for the Preparation of α -Seleno Carbonyl Compounds and Nitriles

[View PDF](#)

Table II. α, β -Unsaturated Aldehydes

[View PDF](#)

Table IIIA. α, β -Unsaturated Acyclic Ketones

[View PDF](#)

Table IIIB. α, β -Unsaturated Cyclobutanones

[View PDF](#)

Table IIIC. α , β -Unsaturated Cyclopentanones

[View PDF](#)

Table IIID. α , β -Unsaturated Cyclohexanones

[View PDF](#)

Table IIIE. α , β -Unsaturated Cycloheptanones and Larger Rings

[View PDF](#)

Table IV. α , β -Unsaturated Carboxylic Acids

[View PDF](#)

Table V. α , β -Unsaturated Carboxylic Esters

[View PDF](#)

Table VIA. α , β -Unsaturated γ -Lactones

[View PDF](#)

Table VIB. α , β -Unsaturated δ -Lactones

[View PDF](#)

Table VIC. α , β -Unsaturated ϵ -Lactones and Larger Rings

[View PDF](#)

Table VII. α , β -Unsaturated Amides and Imides

[View PDF](#)

Table VIIIA. α , β -Unsaturated β -Lactams

[View PDF](#)

Table VIIIB. α , β -Unsaturated γ -Lactams

[View PDF](#)

Table VIII C. α , β -Unsaturated δ -Lactams

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Table VIII D. α , β -Unsaturated ϵ -Lactams and Larger Rings

[View PDF](#)

Table IX. Dehydroamino Acids and Derivatives

[View PDF](#)

Table X. α , β -Unsaturated Nitriles

[View PDF](#)

Table XIA. α , β' -Unsaturated β -Keto Aldehydes

[View PDF](#)

Table XIB. α , β' -Unsaturated β -Diketones

[View PDF](#)

Table XIC. α , β '-Unsaturated β -Keto Esters, Acids, and Lactones

[View PDF](#)

Table XID. α , β '-Unsaturated β -Keto Amides, Lactams, and Nitriles

[View PDF](#)

Table XIE. α , β '-Unsaturated Malonic Acids, Esters, Amides, Nitriles

[View PDF](#)

Table XII. Aromatic Compounds

[View PDF](#)

Table XIII. Miscellaneous

[View PDF](#)

Table I. Methods for Preparing α -Seleno Carbonyl Compounds and Nitriles

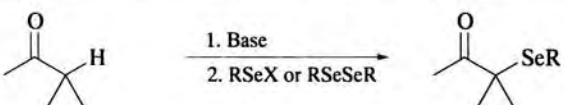
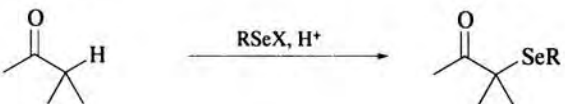
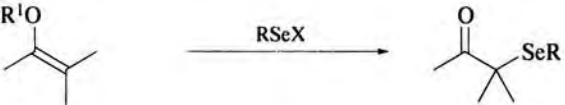

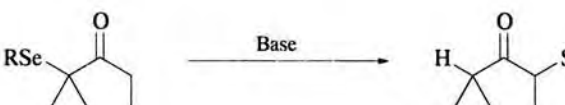
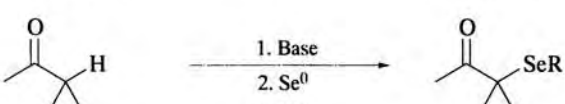
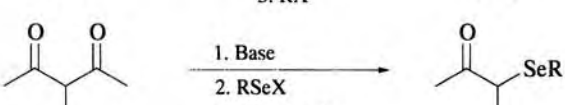
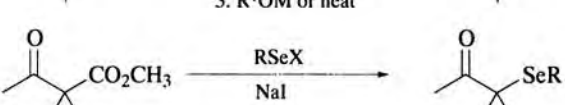
Method	Reaction	Refs.
A-1		2, 3, 4
A-2		3, 47, 65, 236
A-3		2, 4, 100
A-4		164, 360
A-5		246, 248, 249
A-6		61, 62
A-7		361
A-8		362, 363

Table I. Methods for Preparing α -Seleno Carbonyl Compounds and Nitriles (*Continued*)

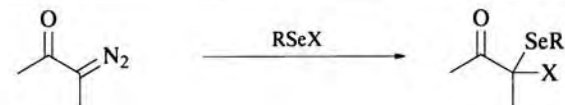
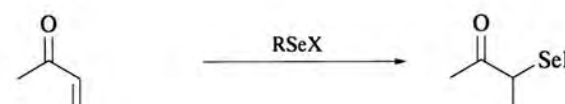
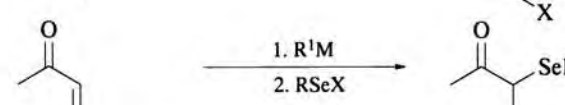
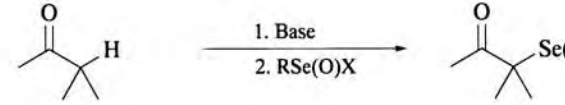
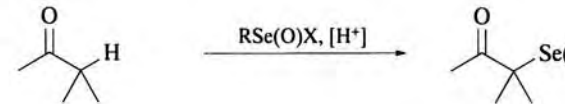
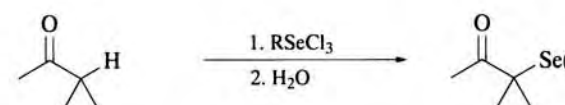
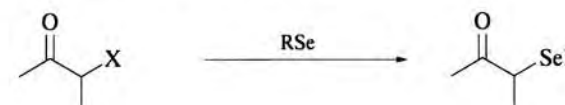
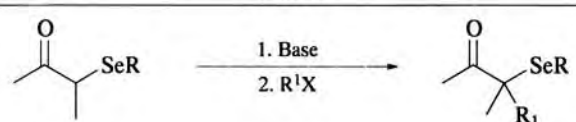
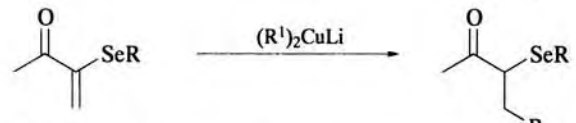
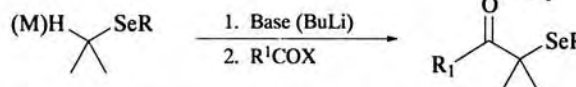
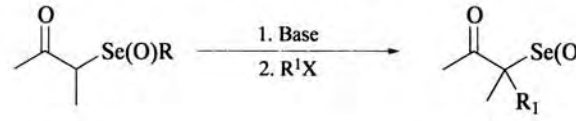
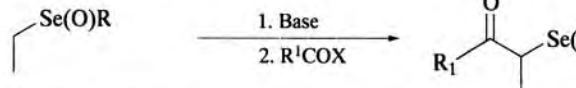
Method	Reaction	Refs.
A-9		155
A-10		145, 146
A-11		2, 242, 252
B. Seleninylations With Electrophilic Reagents.		
B-1		2, 84, 230
B-2		89, 91, 231
B-3		72
C. Reactions With Nucleophilic Reagents.		
C-1		3, 40, 124

Table I. Methods for Preparing α -Seleno Carbonyl Compounds and Nitriles (*Continued*)

D. Carbon-Carbon Bond Forming Reactions of Selenides

Method	Reaction	Refs.
D-1		3, 15, 53, 57, 290, 291, 364
D-2		2, 23, 52, 365
D-3		16

E. Carbon-Carbon Bond Forming Reactions of Selenoxides.

E-1		217
E-2		17

F. Cycloaddition Reactions.


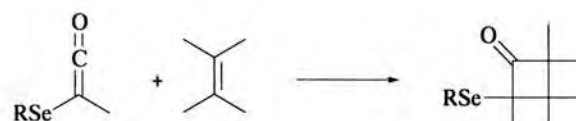
F-1		131-133
F-2		54, 55

Table I. Methods for Preparing α -Seleno Carbonyl Compounds and Nitriles (*Continued*)

G. Miscellaneous Methods

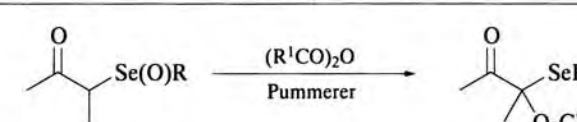
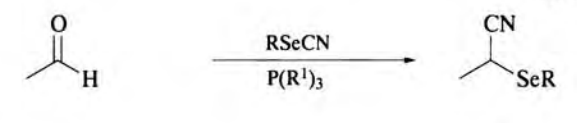
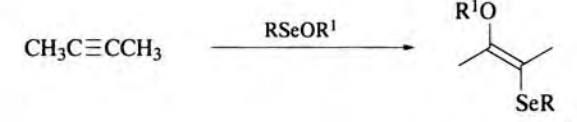
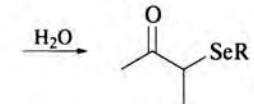
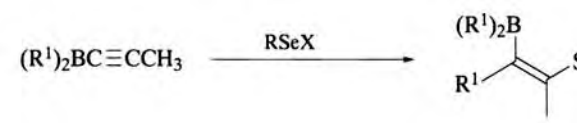
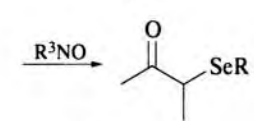
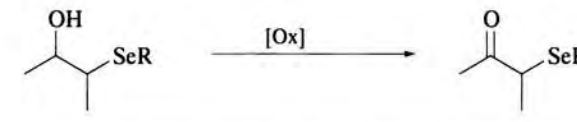
Method	Reaction	Refs.
G-1		158
G-2		37
G-3		63a, 148
		
G-4		149
		
G-5		135

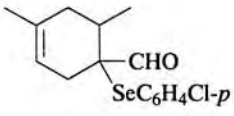
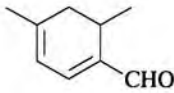
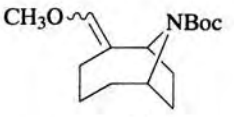
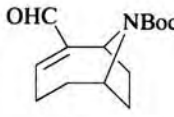
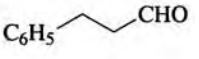
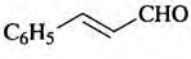
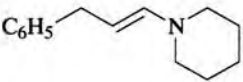
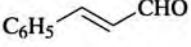
Table II. α,β -Unsaturated Aldehydes

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₅ 	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (89) 2. NaIO ₄ , MeOH, H ₂ O, rt, 1 h	(65)	47
C ₆ 	A-4	1. Piperidine, H ₂ O removed, C ₆ H ₆ 2. PhSeCl, -80° (73) 3. NaIO ₄ , THF, H ₂ O	(—)	366
C ₇ 	A-4	"	(72) <i>E:Z</i> = 98:2	36
<i>n</i> -C ₆ H ₁₃ CHO	A-2	1. 2-PyrSeBr, HCl, EtOH (53) 2. NaIO ₄ , MeOH/H ₂ O (6:1), 23°	<i>(E)</i> - <i>n</i> -C ₄ H ₉ CH=CHCHO (90)	234
	B-3	1. PhSeCl ₃ , ether, rt, 1.5 h; SO ₂ Cl ₂ 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂	" (84)	72
<i>n</i> -C ₅ H ₁₁ CH=CHOTMS	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (85) ^a 2. NaIO ₄ , MeOH, H ₂ O, rt, 1 h	" (90)	47
	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, ether, 25°, 2-3 h 2. NaIO ₄	(67) ^b	164
C ₈ 	A-3	1. PhSeCl, CH ₂ Cl ₂ , K ₂ CO ₃ , -78° (>62) 2. MCPBA, CH ₂ Cl ₂ , -78°, 30 min; <i>i</i> -Pr ₂ NH, 25°	(88)	367

Table II. α,β -Unsaturated Aldehydes (Continued)


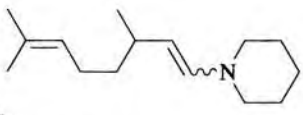
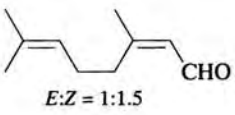
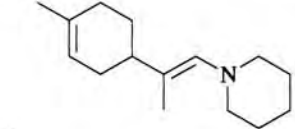
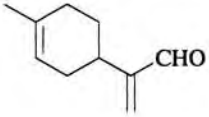
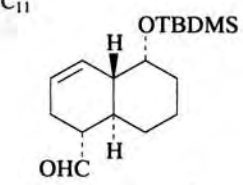
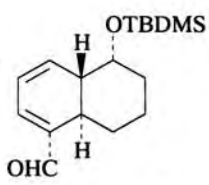
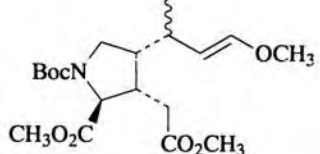
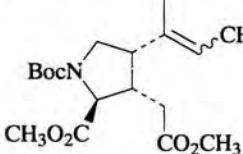
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	F-1	1. CH ₂ =CHCH=CH ₂ , 115° (81) 2. [Ox]	(89)	368, 133
	A-2	1. PhSeNEt ₂ , THF, rt, 16 h (81) 2. H ₂ O ₂ (30%), THF	R = H (94) R = OAc (61)	349
C ₉ 	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, ether, 25°, 2-3 h 2. MCPBA	(60) ^b	164
	F-1	1. CH ₂ =C(CH ₃)CH=CH ₂ , AlCl ₃ , rt (87) 2. [Ox]	(—)	133
	F-1	1. CH ₃ CH=CHCH=CH ₂ (<i>trans</i>), PhMe, reflux (92) 2. [Ox]	(75)	133

Table II. α,β -Unsaturated Aldehydes (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	F-1	[Ox]	 (95)	133
	A-3	1. PhSeCl, CH ₂ Cl ₂ , -30° 2. MCPBA, -78°, 10 min	 (45)	369
	A-2	1. PhSeCl, EtOAc, HCl, 25°, 36 h 2. NaIO ₄ , THF, MeOH, H ₂ O, 25°, 1 h	 (67)	3
	A-2	1. 2-PyrSeBr, EtOH, HCl (64) 2. NaIO ₄ , MeOH/H ₂ O (6:1), 23°	" (83)	234
	B-3	1. PhSeCl ₃ (0.5 eq), ether, rt; SO ₂ Cl ₂ 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂	" (84)	72
	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, ether, 25°, 2-3 h 2. NaIO ₄	 (68) ^b	164

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Table II. α,β -Unsaturated Aldehydes (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (68) ^c 2. NaIO ₄ , MeOH, H ₂ O, rt, 1 h	" (83)	47
	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, ether, 25°, 2-3 h 2. MCPBA	 (44) ^b <i>E:Z</i> = 1:1.5	164
	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, ether, 25°, 2-3 h 2. NaIO ₄	 (50) ^b	164
	A-4	1. Piperidine, H ₂ O removed, C ₆ H ₆ 2. PhSeCl, THF, -110 to -78°, 15 min 3. NaIO ₄ , MeOH, H ₂ O, rt, 14 h	 (84)	360
	A-3	1. PhSeCl, THF, Et ₃ N, H ₂ O (90) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₃ N, rt 2. NBS, THF, 25°, 2 min; H ₂ O, NaOAc, 15 min	 <i>E:Z</i> = 10:1 (30) 39 <i>E:Z</i> = 1:2 (67) 39	39

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Table II. α,β -Unsaturated Aldehydes (Continued)

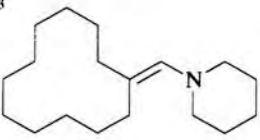
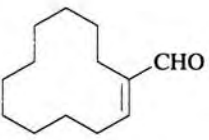
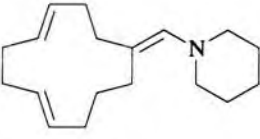
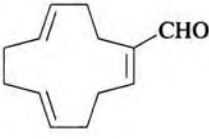
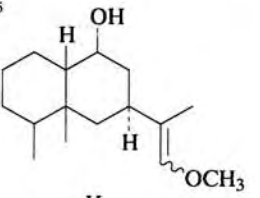
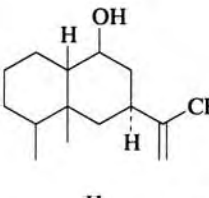
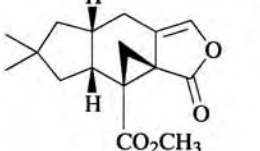
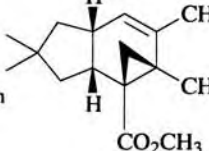
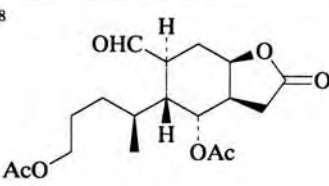
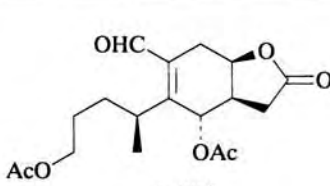
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₂ <i>n</i> -C ₁₁ H ₂₃ CHO	A-2	1. PhSeCl, EtOAc, HCl, 25°, 20 h 2. NaIO ₄ , THF, MeOH, H ₂ O, 25°, 4 h	<i>n</i> -C ₉ H ₁₉ CH=CHCHO (46)	3
C ₁₃ 	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, Et ₂ O, 25°, 2-3 h 2. MCPBA	 (80) ^b <i>E:Z</i> = 1:2	164
C ₁₃ 	A-4	1. PhSeCl, THF, -110°, 5 min; -80°, 15 min; H ₂ O, Et ₂ O, 25°, 2-3 h 2. MCPBA	 (76) ^b <i>E:Z</i> = 1:2	164
C ₁₅ 	A-3	1. PhSeCl, AgO ₂ CCF ₃ , Et ₂ O, 0°; HCl, H ₂ O 2. H ₂ O ₂ (30%), 0° to rt	 (50)	370
C ₁₅ 	A-3	1. PhSeCl, MeOH, 25°, 2 h (92) 2. <i>i</i> -Bu ₂ AlH (5 eq), PhMe/THF (1:1), -78°, 2 h 3. MCPBA, CH ₂ Cl ₂ , -78°; 25°, 4.5 h	 (77)	165

Table II. α,β -Unsaturated Aldehydes (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₈ 	A-2	PhSeCl, (4.4 eq), EtOAc, 60°, 8 h	 (>40) ^d	235

^a The α -phenylselenoaldehyde was also prepared by method A-2 (53%).

^b The yield is overall starting from the aldehyde.

^c The α -phenylselenoaldehyde was also prepared by method A-2 (64%).

^d The yield includes other steps.

Table IIIA. α,β -Unsaturated Acyclic Ketones

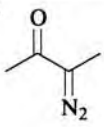
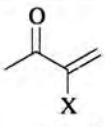
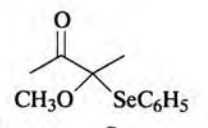
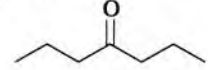
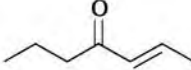
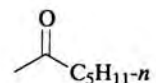
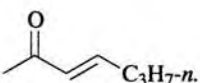
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	A-9	1. PhSeX, CH ₂ Cl ₂ , rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt	 I I X = Cl (79) I X = Br (68) I X = OAc (75)	155
	a	H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	I X = OCH ₃ (54)	155
C ₇ 	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py or 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, heat	 (72)	2
	A-2	1. PhSeCl (4.4 eq), EtOAc, rt, 5 h 2. H ₂ O ₂ (30%), THF, rt, 1 h	" (64)	3
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (95) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (78)	72
	A-2	1. PhSeCl, EtOAc, HCl, rt, 2 h 2. H ₂ O ₂ (30%), THF, rt, 0.5 h	 (34)	3

Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

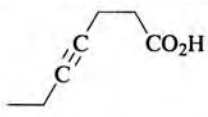
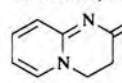
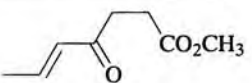
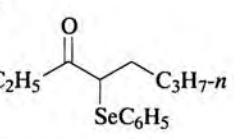
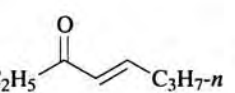
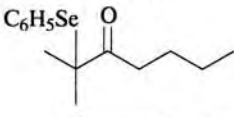
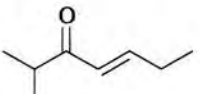
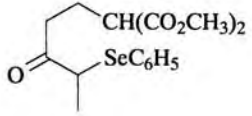
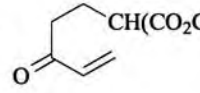
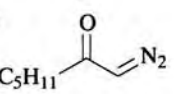
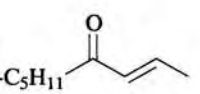
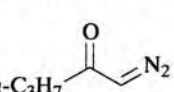
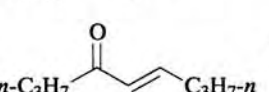
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	G-3	1. PhSeCl, CH ₂ Cl ₂ , -78°;  (83) 2. MeOH, Et ₃ N (90) 3. MCPBA, CH ₂ Cl ₂ , -40°; Py, rt	 (97)	148
C ₈ 	G-4	H ₂ O ₂ (30%)	 (71)	149
	A-5	1. NaH, THF (88) 2. [Ox]	 (95)	246
	A-3	H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0 to 25°	 (72)	132
C ₉ 	—	1. Et ₃ B; PhSeCl, THF, -78° 2. H ₂ O ₂ (15%), THF, Py, 0°	 (74)	239
	—	1. <i>n</i> -Bu ₃ B; PhSeCl, THF, -78° 2. H ₂ O ₂ (15%), THF, Py, 0°	 (90)	239

Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. <i>t</i> -BuOK, <i>t</i> -BuOH, 25°, MeI (71) 2. NaIO ₄ , MeOH, H ₂ O	(54)	371
	A-11	1. (C ₅ H ₉) ₃ B; PhSeCl, THF, -78° 2. H ₂ O ₂ (15%), THF, Py, 0° to rt	(96)	239
	A-1, F	H ₂ O ₂ (15%), CH ₂ Cl ₂ , 0°	(93)	132
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78°, (87) 2. NaIO ₄ , H ₂ O/MeOH (6:1), rt, 90 min or 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py	(89)	2
	A-2	1. PhSeCl, EtOAc, HCl, rt, 35 h 2. NaIO ₄ , THF, MeOH, H ₂ O, rt, 1.5 h	" (84)	3
	A-2	1. 2-PyrSeBr, EtOH, HCl 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	" (97) ^a	234
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (88) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , 0°, 4 h	" (97)	72

Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (89) 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	" (97)	47
	A-2	1. PhSeCl, EtOAc, HCl, rt, 60 h (92) 2. H ₂ O ₂	(81)	321
	A-2	1. PhSeCl, ether, rt, 24 h 2. SO ₂ Cl ₂ ; NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	(8)	72
	A-2	1. PhSeCl, EtOAc, HCl, rt, 35 h (83) 2. NaIO ₄ , THF, MeOH, H ₂ O, rt, 1.5 h	" (92)	2
	B-1	LDA, THF, -78°, 15 min; PhSe(O)Cl, -78°	" (80)	2
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (98) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (87)	72
	A-3	1. AgO ₂ CCF ₃ , PhSeBr, C ₆ H ₆ , rt, 1 min (83) 2. NaIO ₄ , THF, MeOH, H ₂ O, rt, 1.5 h	" (92)	2

Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	E-2	O ₃ , ether, -78°; LDA, THF; PhCO ₂ Me, -78°, 30 min	(81)	17
	A-10	1. PhSeNMe ₂ , CHCl ₃ , rt, 20 h (85) 2. MCPBA, CH ₂ Cl ₂ , -50°; -10°, 30 min	(84) + (2) + (5)	41
	G-4	H ₂ O ₂	(69)	149
	A-2	1. PhSeCl, SO ₂ Cl ₂ , MeOAc, 4 h (36) 2. MCPBA, (2 eq), THF/H ₂ O (5:1), 3 h	(82)	322
R = (CH ₂) ₂ CO ₂ CH ₃				

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Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (89) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	(—)	72
	A-11	1. Me ₂ CuLi, THF, ether, -40°, 5 min; PhSeBr, Ph ₂ Se ₂ 2. MCPBA, -50°; -10°, 30 min	(29) + (63)	41
	A-11	1. Me ₂ CuLi, ether, -40° 2. PhSeBr, Ph ₂ Se ₂ (83) 3. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 30°	(88)	2
	—	1. Et ₃ B; PhSeCl, THF, -78° (96) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 25°, 1 h	(84)	239
	A-10	1. PhSeNMe ₂ , CHCl ₃ , rt, 68 h (94) 2. MCPBA, CH ₂ Cl ₂ , -50°; -20°, 20 min	(54) + (20) + (10)	41

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Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-10	1. AgO ₂ CCF ₃ , PhSeCl, C ₆ H ₆ , rt; NH ₄ OH 2. MCPBA, -50°; -10°, 25 min	(74) + (14)	41
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78°, (87) 2. H ₂ O ₂ (15%), Py, CH ₂ Cl ₂ , 30°	(83)	2, 217
	G-4	H ₂ O ₂ (30%)	(61)	149
	G-4	H ₂ O ₂ (30%)	(75)	149
	—	1. (C ₅ H ₉) ₃ B; PhSeCl, THF, -78° 2. H ₂ O ₂ (15%), THF, Py, 0°	(—)	239

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Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. PhSeCl, THF, -78 to 0° 2. MCPBA, 0°	R = Boc (84) R = BnO ₂ C (85)	372
	A-1	1. LDA, THF, -78°, 15 min; PhSeX 2. H ₂ O ₂ (30%, 6 eq), THF, -10°; <i>i</i> -Pr ₂ NH, CH ₂ Cl ₂ , reflux 5 min	X = Cl, R ¹ , R ² = CH ₂ CH ₂ (73) X = Br, R ¹ , R ² = CH=CH (68)	343
C ₆ H ₅ COC ₅ H _{11-n}	A-2	1. [PhSe] 2. H ₂ O ₂ (30%)	C ₆ H ₅ COCH=CHC ₃ H _{7-n} (75)	373
C ₆ H ₅ SeCH=CH ₂	D-3	1. <i>i</i> -PrLi, ether, 0°; PhCN 2. HCl (5%), 75° 3. [Ox]	C ₆ H ₅ COCH=CHC ₃ H _{7-i} (61)	129
	A-2	1. PhSeCl, EtOAc, HCl, rt 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0° to rt	(>57)	261, 374

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Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, HCl (84) 2. NaIO ₄ , THF/MeOH (6:4), 2 h	(80)	375
	A-1	1. LDA, THF, -78°; PhSeBr, 10 min (79) 2. H ₂ O ₂ , Py	(92)	376
	A-11	1. Me ₂ CuLi, ether, -40°; PhSeBr, -40° to rt 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py	<i>E</i> (21), <i>Z</i> (45)	352
	A-11	1. Me ₂ CuLi, ether, 0°, 10 min; PhSeBr, ether, THF, 25°, 30 min 2. H ₂ O ₂ (30%), AcOH, THF, ether	(55)	377
	A-1	1. LDA, THF, -78°, 10 min; PhSeBr, -78 to 0° 2. H ₂ O ₂ (30%), AcOH, <25°	(85)	1, 2

Table IIIA. α,β -Unsaturated Acyclic Ketones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	G-5	CrO ₃ , H ₂ SO ₄ , THF, H ₂ O, heat 0.5 h	(45)	135
	A-1	1. LDA; PhSeCl (36) 2. H ₂ O ₂ or NaIO ₄	(poor)	190
	A-2	1. PhSeCl, EtOAc, HCl R = H (82), R = Me (quant) 2. MCPBA, CH ₂ Cl ₂ , Na ₂ HPO ₄	R = H (70), R = CH ₃ (89)	378, 379
	A-11	1. Me ₂ C=CHMgBr, CuI, THF, 0°; PhSeBr Ar = C ₆ H ₅ (58) Ar = <i>p</i> -CH ₃ C ₆ H ₄ (35) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	Ar = C ₆ H ₅ (98) Ar = <i>p</i> -CH ₃ C ₆ H ₄ (91)	380, 381, 380

^a The α -methoxy selenide was prepared by methanolysis of the α -bromoselenide.

^b The α -phenylseleno ketone was also formed by method A-1 (69%) and method A-2 (73%).

Table IIIB. α,β -Unsaturated Cyclobutanones

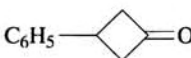
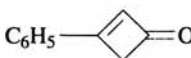
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -100°; PhSeBr, -100° (50) 2. O ₃ , CH ₂ Cl ₂ , -78°	 (53)	1, 2

Table IIIC. α,β -Unsaturated Cyclopentanones

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (77) ^a 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	 R = TMS (85)	47
	A-3	1. PhSeBr, AgO ₂ CCF ₃ , ether, 0° to rt 2. NaIO ₄ , H ₂ O, glyme, rt	" R = Ac (95)	4
	A-2	1. 2-PyrSeBr, HCl, EtOH (52) 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	" (85)	234
	B-3	1. PhSeCl (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (86) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (64)	72, 382
	A-9	1. PhSeX, CH ₂ Cl ₂ , 25° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 25°	 I, X = Cl (82) I, X = Br (73) I, X = OAc (53)	152, 155
	A-9	1. PhSeCl, MeOH, rt	I, X = OCH ₃ (80) ^b	152, 155

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	—	H ₂ O ₂ (15%, 9 eq), Py, CH ₂ Cl ₂ , 0°	 (92)	143
	A-1	1. LDA, THF, -78°, 30 min; PhSeBr, -78 to 25° 2. H ₂ O ₂ (50%), CH ₂ Cl ₂ , Py, 30°	 (41)	383
	A-5	1. NaH, THF, HMPA, 0° to rt (88) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, reflux	" (79)	246
	D-2	1. Me ₂ CuLi, ether, -20° 2. O ₃ , Et ₂ NH, CH ₂ Cl ₂ , heat	 (77)	52
	D-1	1. LDA, THF, -78°; PhSeBr 2. LDA, THF, -78°; CH ₂ O 3. O ₃ , CH ₂ Cl ₂ , -78°	 (—)	384
	A-1	1. LDA, THF; PhSeBr (73) 2. H ₂ O ₂	 (54)	385

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	MCPBA; <i>i</i> -Pr ₂ NH, CH ₂ Cl ₂ , 0 to 23°	(>85)	386
	D-2	1. <i>t</i> -BuNC, TiCl ₄ 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0° to rt, 20 min	(99)	365
	D-2	1. Me ₂ CuLi, ether, -20°; MeX, HMPA 2. O ₃ ; CH ₂ Cl ₂ , Et ₂ NH, heat	(55) + (14)	21,52
		Product from step 1: PhSeLi; PhSeCl; step 2	(4) + (64)	21,52
	A-5	1. LDA (0.5 eq), THF, HMPA, -78° to rt (95) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CH ₂ Cl ₂ , heat	(85)	248

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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-2	1. PhSeBr, Et ₃ N 2. CH ₂ =CHMgBr/CuI 3. MCPBA	(—)	387
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py	(67)	388
	—	H ₂ O ₂ (30%)	R = H, CH ₃ (88-92)	389
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂	(53)	390
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ , AcOH, THF	I, R = H (88)	391, 392

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Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

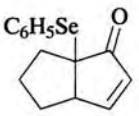
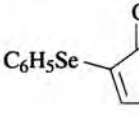
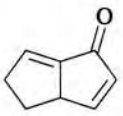
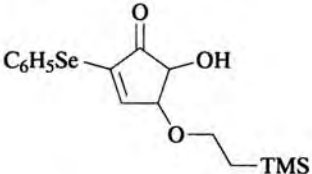
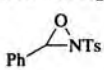
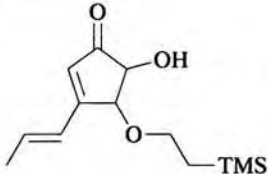
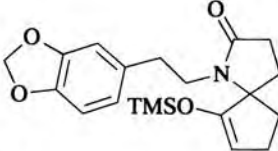
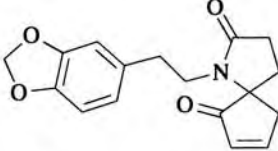
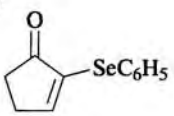
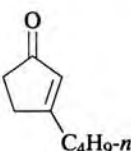
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl (69) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	I, R = CO ₂ CH ₃ (49)	391, 393
	—	MCPBA, CH ₂ Cl ₂ ; Py, 100°, 1 h	 (74)	394
	D-2	1. (<i>E</i>)-CH ₃ CH=CHLi, CuBr•SMe ₂ , -78° 2. 	 (55) ^c	212
	A-3	1. PhSeCl, CH ₂ Cl ₂ , -78° (91) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	 (97)	272
	D-2	1. <i>n</i> -Bu ₂ CuLi, ether, -20° 2. O ₃ ; Et ₂ NH, CH ₂ Cl ₂ , heat	 (94)	52,21

Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

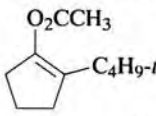
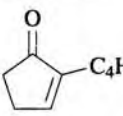
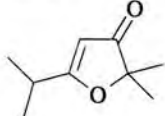
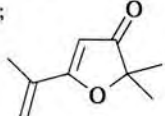
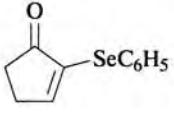
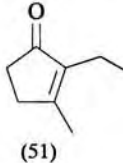
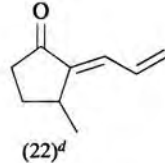
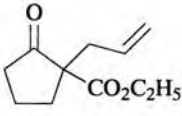
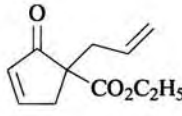
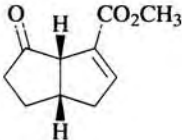
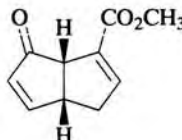
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. CF ₃ CO ₂ Ag, PhSeCl, C ₆ H ₆ (82) 2. O ₃ , -78°; 40°	 (74)	351
	A-1	1. LDA, HMPA, THF, -78°; 45 min; PhSeBr (75) 2. H ₂ O ₂ (30%), THF, 0°, 30 min; rt, 30 min	 (54)	226
	D-2	1. Me ₂ CuLi, ether, -20°; allyl-X, HMPA, 25° 2. O ₃ , CH ₂ Cl ₂ ; Et ₂ NH, heat	 (51) +  (22) ^d	52
		1. Product from step 1: PhSeLi; PhSeCl 2. step 2	(<1) (65)	52
	A-1	1. LDA, PhSeBr, -78° 2. H ₂ O ₂	 (36)	395
	A-2	1. PhSeCl, EtOAc (81) 2. [Ox]	 (40)	225

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -80°, 0.5 h; PhSeBr (54) 2. MCPBA, CH2Cl2, -80 to -60° Et3N	 (57)	225
	D-2	1. <i>n</i> -Bu2CuLi, ether, -20°; MeX, HMPA, 25° 2. O3, CH2Cl2; Et3N, heat	 (50) + (33)	52
		1. Product from step 1: PhSeLi; PhSeCl 2. step 2	(<1) (74)	52
	A-1	1. LDA, THF; PhSeBr R = H (76); R = OTHP (57) 2. H2O2 (30%), THF, AcOH, 0°, 40 min	 R = H (quant) R = OTHP (77)	396
	A-3	1. PhSeBr, -78°, 2 h; 30°, 1 h 2. H2O2 (30%), Py, 5°	 (57) ^e	105

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeX 2. H2O2, THF, Py, 0° to rt	 X R ¹ R ² Br H H (63) Br H H (36) Cl OCH3 H (-) Cl H OCH3 (-)	397 285 398 398
	D-2	1. Me2CuLi, ether, -20°, 20 min, <i>n</i> -C5H11I, HMPA, -20°; rt, 36 h 2. H2O2, (30%), CH2Cl2, 0°, 15 min	 C5H11- <i>n</i> + C4H9- <i>n</i> 65:35 (93)	247
	A-1	1. LDA, THF, -78°; PhSeCl 2. NaIO4, MeOH, THF, H2O, 10°	 (56)	399

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-5	1. LDA (0.5 eq), THF, HMPA, -78° 2. H ₂ O ₂ , CH ₂ Cl ₂	(90)	249
	A-3	1. PhSeBr 2. [Ox]	" (—)	249
	A-5	1. LDA, THF, -78°, 15 min; EtC≡CCH ₂ Br, HMPA, -78° to rt (96) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 30 min	(100)	247
	A-5	1. LDA (0.7 eq), THF, -78°; HMPA, rt, 1 h 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 1 h	(100)	247
	A-1	1. LDA, HMPA, THF, -78°; PhSeBr (84) 2. H ₂ O ₂ (30%), THF, 0° to rt	(70)	226

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. [PhSe] 2. [Ox]	(—)	400
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ , Py, 0°	I , R = C ₂ H ₅ (59) I , R = <i>i</i> -C ₃ H ₇ (47) I , R = Bn (27)	254
	A-1	1. LDA, THF, -78°; PhSeBr 2. MCPBA, Et ₂ NH, THF, -10°	I , R = CH ₂ CH=CH ₂ (26) I , R = CH ₂ CO ₂ CH ₃ (15)	254
	A-3	1. TMSCl, NaI, Et ₃ N, MeCN, 40°; PhSeBr, THF, -78° 2. MCPBA, Et ₂ NH, THF, -10°	I , R = CH ₂ C≡CH (19) I , R = CH ₂ CO ₂ CH ₃ (31)	254
	A-11	1. Ph ₂ CuLi; PhSeBr, Ph ₂ Se ₂ (55) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 10°	(72)	217

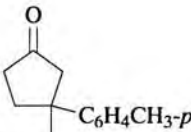
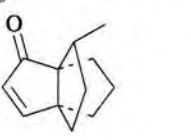

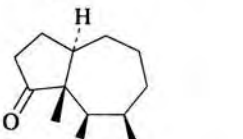
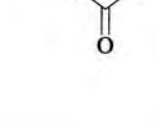
Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), THF, AcOH	(50)	337
	A-2	1. [PhSe] 2. [Ox]	(>42)	401
	A-1	1. LDA, THF, -78°; PhSeBr, -78°, 10 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt, 2 h	(>43)	402
	A-1	1. LDA, THF, -78°, 15 min; PhSeCl 2. H ₂ O ₂ (30%), THF, -10°; <i>i</i> -Pr ₂ NH, CH ₂ Cl ₂ , reflux	(62)	343
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 30°	(66)	2,217

Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

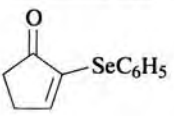
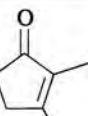
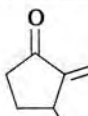
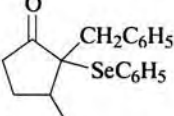
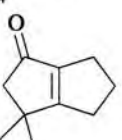
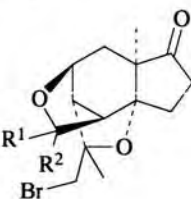
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-5	1. NaH, THF, HMPA, 0° to rt (82) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, reflux	" (88)	246
	A-3	1. AgO ₂ CCF ₃ , PhSeBr, C ₆ H ₆ , rt, 1 min (96) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 30°	(95) A:B = 44:56	2,217
	A-11	1. (<i>n</i> -Bu ₂ Li) ₂ •CuCN (1.5 eq), ether, -78°; PhSeBr (4 eq) (82, 4:1 isomer ratio) 2. H ₂ O ₂ , CH ₂ Cl ₂ , H ₂ O	(—) <i>E</i> : <i>Z</i> = 1:1	403
	A-11	H ₂ O ₂ (30%), THF, NH ₄ Cl, NH ₃	(>70)	244
	A-2	1. PhSeCl, EtOAc, rt 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, rt	R ¹ = R ² = H (47)	404

Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LiTMP, THF, -78°; PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0° to rt	" R ¹ , R ² = =O (93)	405
	A-2	1. PhSeCl, CH ₂ Cl ₂ (65) 2. H ₂ O ₂ , HOAc, CH ₂ Cl ₂	(42)	406
	A-11	1. MeMgI, CuBr, ether, THF, -78 to 0°; PhSeBr, THF, HMPA, 0°, 30 min 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 25°, 2 h	(-)	402
	A-1	1. LDA, PhSeCl, THF, -78° (82) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	(82)	407
	A-2	1. PhSeCl, EtOAc, 20°, 3 h (74) 2. O ₃ , CH ₂ Cl ₂ , -78°; Py, 30°, 15 min	(74)	408

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Table III.C. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-2	1. Me ₂ CuLi, ether, -20°; PhCH ₂ X, HMPA, 25° 2. H ₂ O ₂ , CH ₂ Cl ₂ ; Et ₂ NH, heat	 +  (9) (53)	52
		1. Product from step 1: PhSeLi; PhSeCl 2. step 2	(<1) (69)	52
	A-5	1. LDA (0.5 eq), THF, HMPA, -78° to rt (92) 2. O ₃ , CH ₂ Cl ₂ -78°; Et ₂ NH, heat	(77)	248
	A-11	1. CH ₂ =CH(CH ₂) ₂ MgBr, CuBr•SMe ₂ , THF, -78° to rt; PhSeBr, THF/HMPA (3:1), 0°, 10 min (64) 2. H ₂ O ₂ (5%), CH ₂ Cl ₂ , Py, rt, 30 min	(64)	243
	A-2	1. PhSeCl, EtOAc, HCl, rt 2. H ₂ O ₂ (30%), EtOAc, rt	R ¹ , R ² = =O (73) ^f	409

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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), 0° to rt	" R ¹ = H, R ² = OCH ₃ (63)	409
	A-1	1. LDA, THF, -78°, 1 h; PhSeCl, -78°; (88) 2. MCPBA, CH ₂ Cl ₂ , -78°; Et ₃ N, -5° to rt	(44)	410, 411
	A-1	1. [Kinetic selenenylation] 2. [Ox]	(64)	412
	A-2	1. PhSeCl, rt, 3 h 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt, 45 min	(78)	413, 414, 414a
	A-2	1. PhSeCl, EtOAc, HCl 2. NaIO ₄	(—)	98

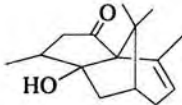
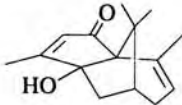
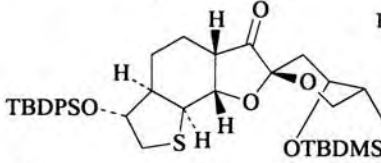
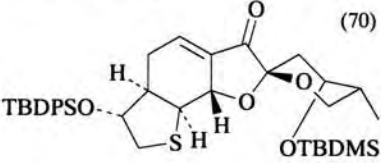
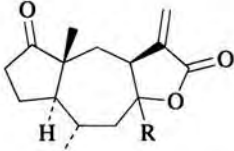
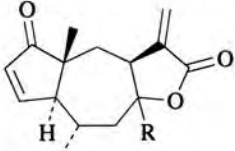
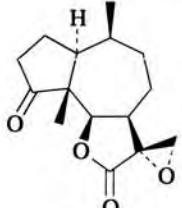
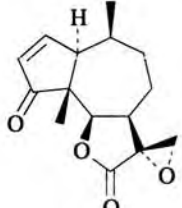
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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.																																				
	A-2	1. PhSeCl, EtOAc, rt, 4 h (100) 2. NaIO ₄ , <i>t</i> -BuOH, rt; 60°, 2 h	(41)	260, 415																																				
	A-2	1. PhSeCl (2 eq), EtOAc, 50°, 1 h (90) 2. O ₃ , CH ₂ Cl ₂ , -72° 3. CH ₂ =CHOAc, KOAc, AcOH, rt, 17 h	(95)	179																																				
	A-1	1. LDA, THF, -78°; PhSeX, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, 0°																																						
			<table border="1"> <thead> <tr> <th>R¹</th> <th>R²</th> <th>R³</th> <th>X</th> <th></th> <th></th> </tr> </thead> <tbody> <tr> <td>H</td> <td>OTHP</td> <td>CH₃</td> <td>Cl</td> <td>(50)</td> <td>416</td> </tr> <tr> <td>H</td> <td>OTHP</td> <td>CH₃</td> <td>Cl</td> <td>(>50)</td> <td>417</td> </tr> <tr> <td>H</td> <td>OH</td> <td>CH₃</td> <td>Cl</td> <td>(35)</td> <td>418,419</td> </tr> <tr> <td>OH</td> <td>OTHP</td> <td>CH₃</td> <td>Br</td> <td>(>65)</td> <td>420</td> </tr> <tr> <td>H</td> <td>H</td> <td>CO₂CH₃</td> <td>Cl</td> <td>(51)</td> <td>421</td> </tr> </tbody> </table>	R ¹	R ²	R ³	X			H	OTHP	CH ₃	Cl	(50)	416	H	OTHP	CH ₃	Cl	(>50)	417	H	OH	CH ₃	Cl	(35)	418,419	OH	OTHP	CH ₃	Br	(>65)	420	H	H	CO ₂ CH ₃	Cl	(51)	421	
R ¹	R ²	R ³	X																																					
H	OTHP	CH ₃	Cl	(50)	416																																			
H	OTHP	CH ₃	Cl	(>50)	417																																			
H	OH	CH ₃	Cl	(35)	418,419																																			
OH	OTHP	CH ₃	Br	(>65)	420																																			
H	H	CO ₂ CH ₃	Cl	(51)	421																																			

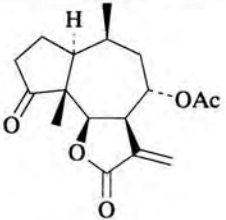
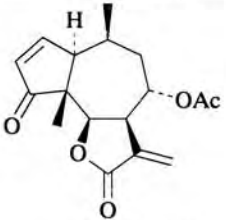
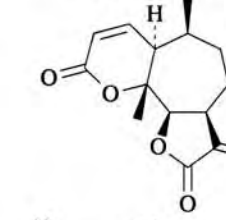
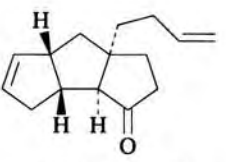
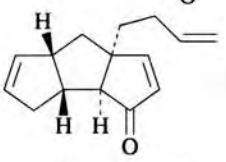
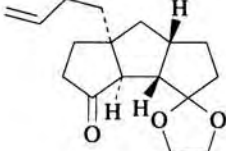
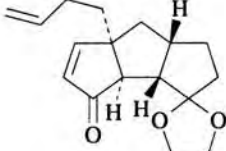
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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. LDA, TMSCl; PhSeCl 2. H ₂ O ₂ , K ₂ CO ₃ , MeOH	 (95)	104
	B-1	1. LDA, THF, HMPA, 0° 2. PhSe(O)Cl	 (70)	84
	—	1. [PhSe] 2. [Ox]	 R = α -H (52)	422, 423
	A-2	1. PhSeCl, EtOAc, HCl 2. NaIO ₄ , THF, H ₂ O, 25°, 7 h	" R = β -H (~75)	276
	A-2	1. PhSeCl, Dowex 50-X8 (H ⁺), EtOAc (77) 2. NaIO ₄ , THF/H ₂ O (6:1)	 (60)	271

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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt 2. H ₂ O ₂ (30%)	 (55) ^y +  (42) ^y	198
	A-1	1. LiN(TMS) ₂ , THF; PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0 to 20°	 (48)	424
	A-1	1. LiN(TMS) ₂ , THF; PhSeCl, -78 to 25° 2. H ₂ O ₂ , THF, rt	 (85)	425

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Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl (2 eq), EtOAc, 50°, 1 h (69) 2. O ₃ , CH ₂ Cl ₂ , -72° 3. CH ₂ =CHOAc, KOAc, AcOH or 3. Et ₂ NH, rt, overnight; reflux 10 min or 3. CH ₂ =CHOAc, CF ₃ CH ₂ OH, K ₂ CO ₃ , rt, 4 h	 I, Nu = OAc (47)* I, Nu = N(C ₂ H ₅) ₂ (—)* I, Nu = OCH ₂ CF ₃ (43)*	179
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (35%), Py, CH ₂ Cl ₂	 R = CH ₂ C=C(CH ₂) ₅ OTHP (55) R = (CH ₂) ₈ OTHP (65)	426
	A-2	1. PhSeCl, EtOAc (47) 2. [Ox]	 (—)	427

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. LDA, THF, -78°, 15 min; PhSeCl, -78° to rt (26) 2. H ₂ O ₂ (15%), Py, CH ₂ Cl ₂ , rt, 2 h	 (62)	270
	A-1	1. TMSCl, LDA, THF, -78°; PhSeCl, Py, THF, -78° (90) 2. MCPBA, 0°; NaHCO ₃ ^h 3. CCl ₄ , reflux	 (80) ⁱ	35
	G-1	1. MCPBA, CH ₂ Cl ₂ , 0°; NaHCO ₃ ^h 2. Ac ₂ O, Py 3. H ₂ O ₂ , CCl ₄	 (60) ^j	35
	A-1	1. LDA (2.2 eq), THF, -78°, 1 h; PhSeCl (3 eq) 2. NaIO ₄ , H ₂ O, MeOH, rt; H ₃ O ⁺	 (41)	428

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	—	1. O ₃ , CH ₂ Cl ₂ , -78° 2. CF ₃ CH ₂ OH, CH ₂ =CHOEt, KOAc	 R =	(39) ^g 221
	—	1. MCPBA, CH ₂ Cl ₂ , -70° 2. CF ₃ CH ₂ OH, Et ₃ N, -70° to rt	 R =	(51) ^{e,g} 221
	A-1	1. LDA; PhSeBr 2. H ₂ O ₂ ; heat		(49) 429

Table IIIC. α,β -Unsaturated Cyclopentanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, 50° (60) 2. MCPBA, CH ₂ Cl ₂		(79) ^g 221

^a The α -phenylseleno ketone was also prepared by method A-1 (53%) and method A-2 (52%).

^b No oxidation was required.

^c Oxidation with hydrogen peroxide gave the enone in 10% yield; with MCPBA, 25%.

^d The leaving group X was not specified.

^e The yield includes other steps.

^f The yield was calculated by the authors.

^g The intermediate enone was trapped by conjugate addition.

^h The selenoxide is stable at room temperature.

ⁱ The product is contaminated by some material silylated on the acetoxy group, which can be removed with *n*-Bu₄NF at the selenide stage.

Table IIID. α,β -Unsaturated Cyclohexanones

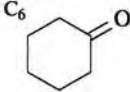
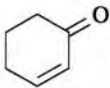
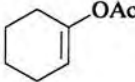
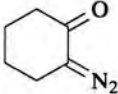
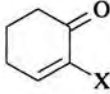
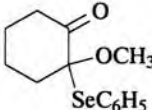
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. 2-PyrSeBr, HCl-H ₂ O (36.5%), EtOH, reflux 0.5 h (89) ^a 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	 (82)	47, 234
	A-2	1. PhSeCl, EtOAc, rt, 0.5 h (80) 2. NCS, MeOH/CH ₂ Cl ₂ (1:1), 0°, 30 min; NaOH (10%) or 2. <i>t</i> -BuOCl, MeOH/CH ₂ Cl ₂ (1:1), 0°, 5 min; NaHCO ₃ , H ₂ O, 5 min	" (74)	215
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (92) ^b 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (47)	72, 382
	A-3	1. PhSeBr, Ag ₂ OCCF ₃ , ether, 0° to rt; H ₂ O, THF, HCl (70) 2. NaIO ₄ , H ₂ O, glyme, rt	" (92)	4
	A-9	1. PhSeX, CH ₂ Cl ₂ , rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt	 I	I, X = Cl (82) I, X = Br (83) I, X = OAc (68)
	c	H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	I, X = OCH ₃ (67)	155, 152

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

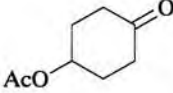
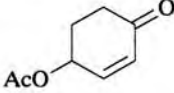
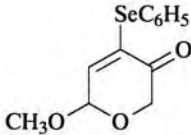
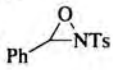
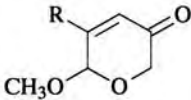
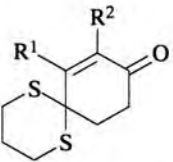
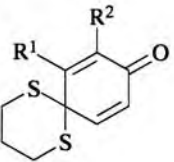
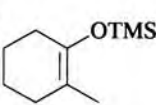
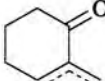
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.	
	A-2	1. PhSeCl, EtOAc, rt, 1 h 2. H ₂ O ₂ (30%), THF, 35°, 1 h or 2. NaIO ₄ , THF, MeOH, H ₂ O, rt, 0.75 h	 (53)	3	
	D-2	1. A 2. 		211	
		A = Me ₂ CuLi, ether, -78° A = <i>i</i> -PrMgBr, CuBr•SMe ₂ , THF, -10° to rt	R = CH ₃ (48) R = <i>i</i> -C ₃ H ₇ (25)		
	A-1	1. LDA, THF, -78°; PhSeBr 2. MCPBA, CH ₂ Cl ₂ , <0°		$\begin{matrix} R^1 & R^2 \\ H & H \\ H & CH_3 \\ C_6H_5 & H \end{matrix}$ (43) (25) (36)	430
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (83) ^d 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	 <i>exo:endo</i> = 32:68 (79)	47	

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-2	1. Me ₂ CuLi, ether, -20° 2. O ₃ , CH ₂ Cl ₂ ; Et ₂ NH, heat	 (76)	52,21
	A-2	1. EtOAc, rt, 2 h 2. H ₂ O ₂ (30%), 30°, 2 h	 (91) ^e	431
	A-2	1. , THF, 0° (44) 2. H ₂ O ₂ (30%), THF, rt -	" (-100) ^f	99
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min (41) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	 (76)	72
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (73)	2
	A-1	1. LDA, THF, -78 to 40°, 2 h; 2-PyrSeBr, -65° to rt, 0.5 h (87) ^g 2. O ₃ , CH ₂ Cl ₂ , -78°; CCl ₄ , reflux	" (90)	47

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-9	1. PhSeX, CH ₂ Cl ₂ , rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt	 X = Cl (88) X = Br (72) X = OAc (75)	155
	E-1	O ₃ , ether, -78°; LDA, -78°; PhSeCl, -78°; rt	 (57)	217
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂	 (—)	432
	D-2	1. Me ₂ CuLi, ether, -20°; MeX, HMPA, 25° 2. O ₃ , CH ₂ Cl ₂ ; Et ₂ NH, heat	 (51) + (22)	52
		1. Product from step 1: PhSeLi; PhSeCl 2. step 2	 (60) + (14)	52

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

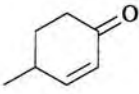
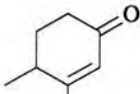
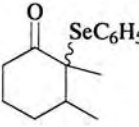
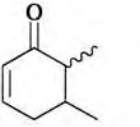
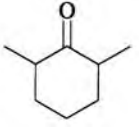
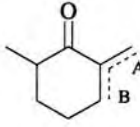
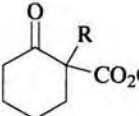
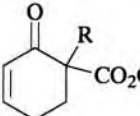
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-11	1. Me_2CuLi , ether, -40° ; PhSeBr , Ph_2Se_2 , (87) 2. O_3 , CH_2Cl_2 , -70° ; Et_2NH , CCl_4 , reflux	 (59)	167
	A-5	1. LDA (0.5 eq), HMPA, THF, -78° to rt (100) 2. O_3 , CH_2Cl_2 , -78° ; Et_2NH , heat	 (90)	248
	A-1	1. LDA, THF, -78° ; PhSeBr , -78° 2. H_2O_2 , AcOH, $<25^\circ$ (one pot) or 2. H_2O_2 , MeOH	 A: B: (69) A:B = 67:33 (76)	1
	A-2	1. PhSeCl , EtOAc 2. H_2O_2 , THF	 R = CH_3 (55-65) R = C_2H_5 (55-65)	433

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

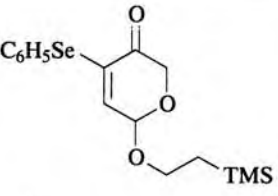
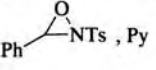
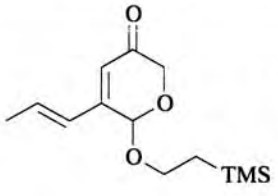
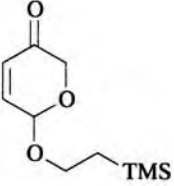
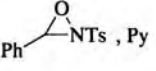
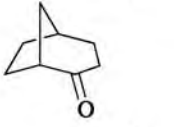
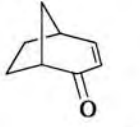
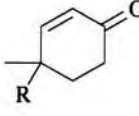
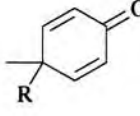
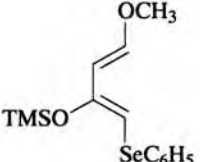
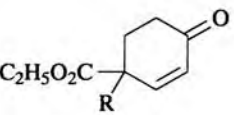
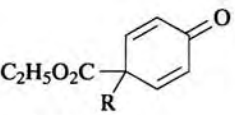
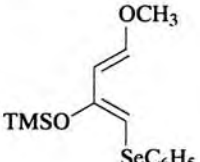
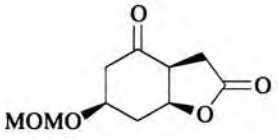
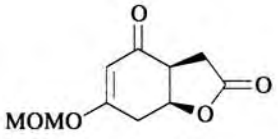
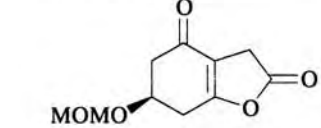
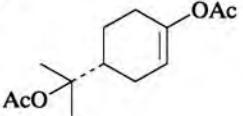
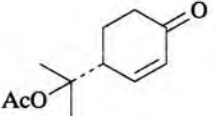
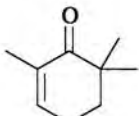
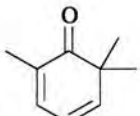
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-2	1. (<i>E</i>)- $\text{CH}_3\text{CH}=\text{CHLi}$, $\text{CuBr}\cdot\text{SMe}_2$, -78° (64) 2.  , Py	 (57)	212
	A-11	1. (<i>E</i>)- $\text{CH}_3\text{CH}=\text{CHLi}$, $\text{CuBr}\cdot\text{SMe}_2$, -78° (64) 2. PhSeCl (21) 3.  , Py	" (57)	212
	A-1	1. LDA, THF, -78° , 15 min; PhSeBr , -78° (80) 2. H_2O_2 (15%), Py, CH_2Cl_2	 (72)	2
	A-1	1. LDA, THF, -78° , 10 min; PhSeCl , -78 to 0° 2. H_2O_2 (30%), THF, 25° , 1.5 h; NaHSO_3	 I, R = CH_3 (83)	434

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt, 2.5 h (69) 2. H ₂ O ₂ (30%), EtOAc, 20°	I, R = CH ₃ (75)	259
	A-2	1. PhSeCl, EtOAc, rt, 5 h (72) 2. H ₂ O ₂ (30%), EtOAc, 15°, 2 h	I, R = C ₆ H ₅ (92)	259
	A-2	1. PhSeCl 2. H ₂ O ₂	I, R = CN (42)	435
	F-1	1. CH ₂ =C(CH ₃)COCl, C ₆ H ₆ , reflux; MeOH, Py 2. H ₂ O ₂ (15%), MeOH, CH ₂ Cl ₂ , Py, 0°	I, R = CO ₂ CH ₃ (29)	131, 436
	F-1	1. CH ₂ =C(CH ₃)CO ₂ CH ₃ , C ₆ H ₆ , 120°, 24 h 2. HCl, H ₂ O, THF (16) 3. [Ox]	I, R = CO ₂ CH ₃ (91)	131, 436
	A-2	1. PhSeCl, EtOAc, rt, 2.5 h R = CH ₃ (78), R = C ₂ H ₅ (78), R = CH ₂ CO ₂ C ₂ H ₅ (65) R = n-C ₃ H ₇ (70), R = C ₆ H ₅ (68) 2. H ₂ O ₂ (30%), EtOAc, 10 to 20°	 I I, R = CH ₃ (85) I, R = C ₂ H ₅ (78) I, R = CH ₂ CO ₂ C ₂ H ₅ (75) I, R = n-C ₃ H ₇ (85) I, R = C ₆ H ₅ (83)	259

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Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	F-1	1. CH ₂ =C(C ₆ H ₅)COCl, C ₆ H ₆ , 115°, 24 h 2. HCl (0.005 N), NH ₄ Cl 3. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°	I, R = C ₆ H ₅ (50)	131, 436
	A-2	1. PhSeCl, EtOAc, 2. H ₂ O ₂	 (85) +	437
			 (<10)	
	A-3	1. AgO ₂ CCF ₃ , C ₆ H ₆ , PhSeBr 2. H ₂ O ₂ , THF, rt	 (—)	438
	A-1	1. LDA, THF, -78°, 0.5 h; PhSeCl (40) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt	 (10)	439

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Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

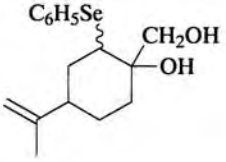
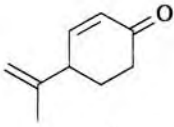
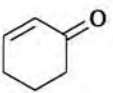
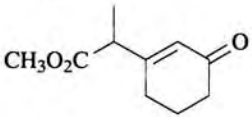
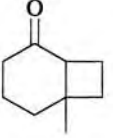
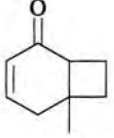

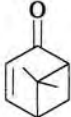
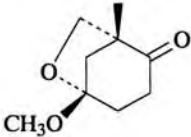
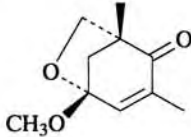
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	—	NaIO ₄ , THF, H ₂ O, 25°	 (60-70)	440
	A-11	1. CH ₃ CH=C(OCH ₃)OTMS, MeCN, 55°, 3.5 h (96) 2. PhSeCl, CH ₂ Cl ₂ , 25°, 15 min 3. MCPBA (2.7 eq), CH ₂ Cl ₂	 (51)	252
	A-2	1. PhSeCl, EtOAc; HO(CH ₂) ₂ OH, TsOH 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py; 1 N HCl, ether	 (45)	441
	A-1	1. LDA, THF, -78°, 2 h; PhSeBr, -78°, 30 min 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py; 0°, 0.5 h	 (—)	442
	D-1	1. LiN(TMS) ₂ , THF, -78°; PhSeBr 2. NaH, THF, 0°; CH ₃ I (93) 3. H ₂ O ₂ (35%), THF, NaHCO ₃	 (65)	353

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

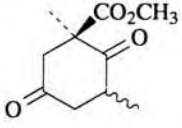
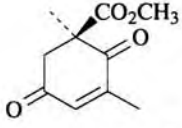
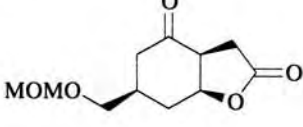
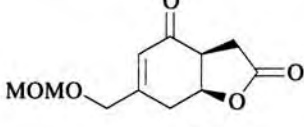
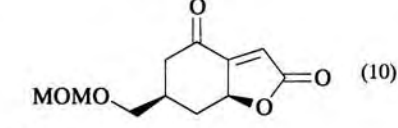
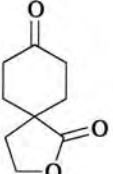
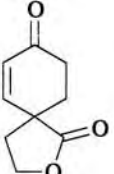
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc 2. H ₂ O ₂	 (79)	443, 444
	A-2	1. PhSeCl, EtOAc, rt, overnight 2. H ₂ O ₂ (30%), THF, EtOAc, 0°, 1 h	 (82) +  (10)	268
	A-2	1. PhSeCl, EtOAc, rt, 35 min (54) 2. H ₂ O ₂ (30%), THF, EtOAc, rt, 1 h	 (72)	259

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt, 7 h (62) 2. H ₂ O ₂ (30%), EtOAc, 5°, 1.5 h	(87)	259
	A-1	1. LDA, THF; PhSeBr 2. H ₂ O ₂ , CH ₂ Cl ₂	(—)	445
	A-2	1. PhSeCl, EtOAc, 0.25 h 2. H ₂ O ₂ (30%), THF, 35°, 0.75 h or 2. CH ₃ CO ₃ H	(74)	3
	A-2	1. NHSeC ₆ H ₅ , THF, 0° (44) 2. H ₂ O ₂ (30%), THF, rt	" (~100) 21% ee	99
	B-3	1. PhSeCl ₃ (0.5 eq), ether, 0°, 20 min; SO ₂ Cl ₂ (83) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (68)	78, 382

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	—	CH ₃ CO ₃ H, HCl, EtOAc	(63)	199
	D-2	1. (<i>n</i> -C ₄ H ₉) ₂ CuLi (90) 2. O ₃ ; Et ₂ NH	(85)	21
	A-1	1. LDA, THF, -70°; PhSeBr 2. H ₂ O ₂ (30%), THF, <i>i</i> -Pr ₂ NH	(24)	446
	A-1	1. LDA, THF, -78°; PhSeBr (87) 2. NaIO ₄ , H ₂ O, MeOH	I R = H (82)	447
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂	I R = CH ₃ (51)	448
	A-1	1. LDA, THF, -78° (60) 2. H ₂ O ₂ , Py, THF, 0° to rt	I R = H (76)	214

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

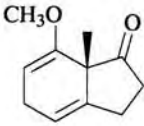
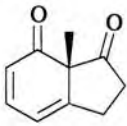
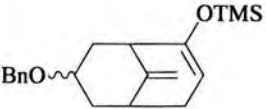
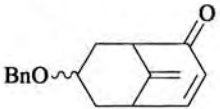
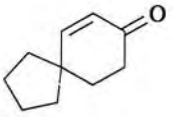
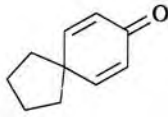
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78° (60) 2. Chloramine-T, $\text{BnN}^+\text{Et}_3\text{Cl}^-$, H_2O , CH_2Cl_2 , 15 min, rt	I R = H (95)	214
	A-1	1. LDA, THF, -78°; PhSeBr 2. H_2O_2 (30%)	I R = CH_3 (61)	449
	B-2	1. $(\text{PhSeO})_2\text{O}$, PhCl, 90°	I R = CH_3 (94)	449
	A-3	1. PhSeCl, H_2O (2.2 eq), DMSO 2. H_2O_2 (10 eq), CDCl_3 , 0°	 (—) ^h	170
	A-3	1. PhSeCl, THF 2. H_2O_2 (15%), CH_2Cl_2 , rt	 (>50)	450
	B-2	$(\text{PhSeO})_2\text{O}$ (0.1 eq), <i>m</i> -iodoxybenzoic acid, PhMe, reflux 3 h	 (70)	89,92
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78 to 0° 2. H_2O_2 (30%), THF, 25°, 1.5 h; NaHSO_3 , 30 min	" (96)	434

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

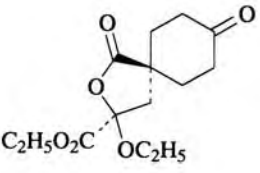
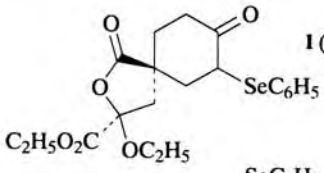
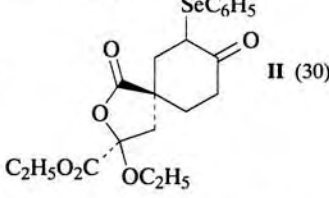
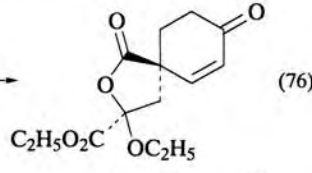
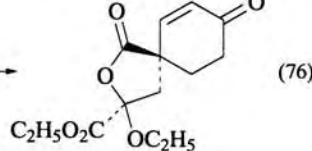
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, 2.5 h, (separate I and II)	 I (33)	451, 452
			+  II (30)	
		2. H_2O_2 (30%), EtOAc	I \rightarrow  (76)	
			II \rightarrow  (76)	

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

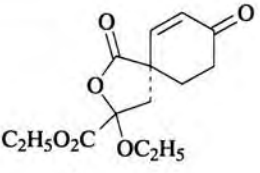
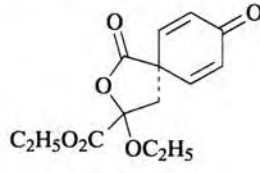
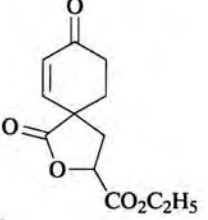
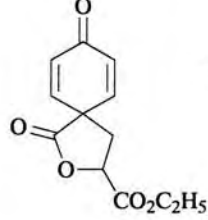
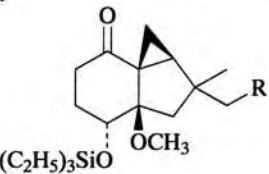
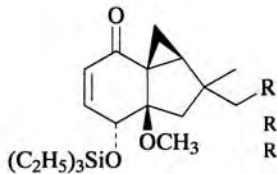
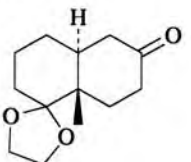
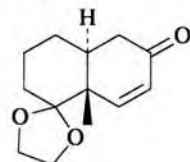
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, 10 h, (71) 2. H ₂ O ₂ (30%), EtOAc, 5°, 50 min	 (31)	171, 452
	A-2	1. PhSeCl, EtOAc, rt, 6 h, (70) 2. H ₂ O ₂ (30%), EtOAc, 10°, 2.5 h	 (82)	259
	A-1	1. LDA, PhSeCl 2. H ₂ O ₂ (30%)	 R = H (60) R = OBn (>51)	453 454
	A-2	1. PhSeCl, EtOAc 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	 (—)	263

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

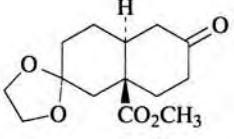
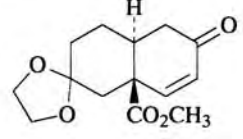
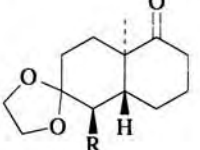
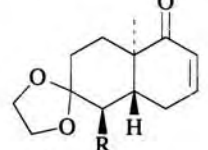
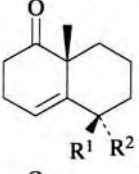
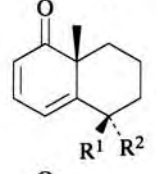
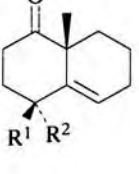
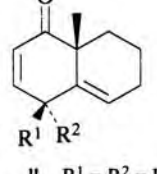

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt, 3 h 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, rt	 (40)	264
	A-1	1. LDA, THF, -78°; PhSeCl R = H (89), R = CH ₃ (93) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°	 R = H (77) R = CH ₃ (83)	455, 456
	A-1	1. LDA (2 eq), THF, -60 to -70°, 1 h; PhSeBr, THF, -70°, 2.5 h 2. H ₂ O ₂ (30%), THF, rt, 1 h	 R ¹ = OH, R ² = H (78) R ¹ = H, R ² = OH (73)	457
	A-1	1. LDA (2 eq), THF, -60 to -70°; PhSeBr 2. H ₂ O ₂ (30%), THF, rt, 1 h	 R ¹ = OH, R ² = H (60) R ¹ = H, R ² = OH (52)	457
	A-1	1. LDA, THF, -70°; PhSeBr 2. H ₂ O ₂ (30%), THF	" R ¹ = R ² = H (72)	457

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O, PhCl, reflux 30 min	R = COCH ₃ (70)	169, 277
	B-2	(PhSeO) ₂ O, C ₆ H ₆ , 72 h	" R = COCF ₃ (60)	169, 277
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	(90)	458
	B-2	Ph ₂ Se ₂ (0.02 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (3 eq), PhMe, reflux 3 h	(87)	89,92
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, 25°, 1.5 h; NaHSO ₃	" (96) ^f	434
	A-1	1. LDA, THF, -78° PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, 25°; NaHSO ₃	(96)	434

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; PhSeBr (87) 2. H ₂ O ₂ (30%, 8 eq), 2 M NaOH, H ₂ O, MeOH, 0 to 25°, 5 h	(76)	447
	A-5	1. LDA (0.5 eq), HMPA, THF, -78° to rt (100) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, heat	(90)	248
	A-2	1. PhSeCl, EtOAc, 5 to 10° 2. H ₂ O ₂ (30%), 0° to rt	(75)	326
	A-3	1. PhSeCl, C ₆ H ₆ , 0 to 20° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	(95)	49

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -70°, 40 min; PhSeCl 2. H ₂ O ₂ (30%), EtOAc, rt, 3 h	(52)	459
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78°, 3 h (88) 2. H ₂ O ₂ (30%), THF, 0 to 15°, 5 h	(78)	460, 461
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, 0°	(20)	339
	A-1	1. LDA; PhSeBr 2. NaIO ₄	(—)	462, 463

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), THF, -10°; <i>i</i> -Pr ₂ NH, heat	(73)	343
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ (30%), THF, -10°; <i>i</i> -Pr ₂ NH, heat	(68)	343
	A-2	1. PhSeCl, EtOAc, rt, 2 h 2. MCPBA, NaHCO ₃	(91)	258
	A-3	1. TMSOTf, Et ₃ N; PhSeCl, THF, 0° 2. <i>n</i> -Bu ₄ NF, -78° (71) 3. H ₂ O ₂ , CH ₂ Cl ₂ , 0°	+	R = H, 85:15 (65) 48 R = TMS, 85:15 (63) 253

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

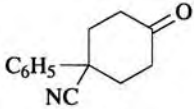
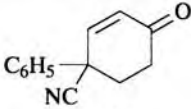
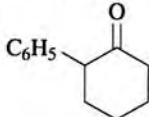
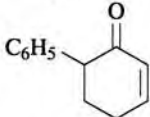
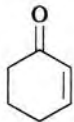
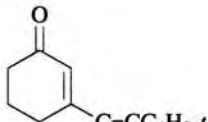
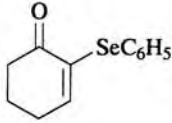
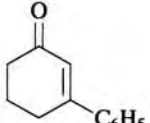
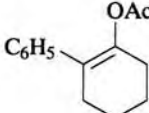
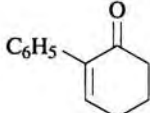
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, 0°; PhSeCl, -78° (50) 2. H ₂ O ₂ (30%), MeOH, rt	 (35)	314
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° 2. H ₂ O ₂ (15%), Py, CH ₂ Cl ₂ , 5° or 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (60) " (62)	2,217 2
	A-11	1. <i>t</i> -BuC=CAI(Me)OMe, [Ni], ether, C ₆ H ₆ , PhSeBr, Ph ₂ Se ₂ , -78° 2. H ₂ O ₂ (30%), THF, NH ₄ Cl, NH ₃	 (66)	244
	D-2	1. Ph ₂ Cu(CN)Li, Et ₂ O, -78° (65) 2. H ₂ O ₂	 (—)	23
	A-1	1. MeLi, THF, -20 to 0°, 10 min; PhSeBr, -78° (86) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py	 (94)	2,217

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

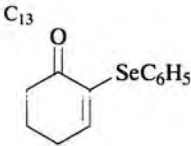
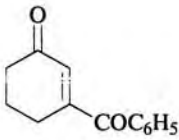
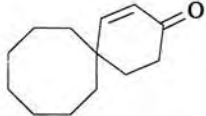
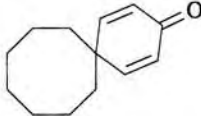
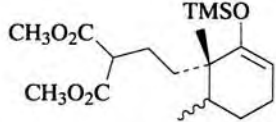
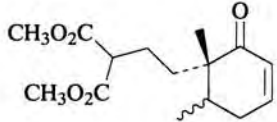
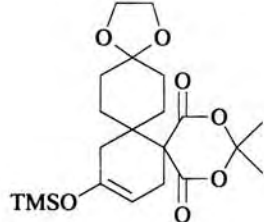
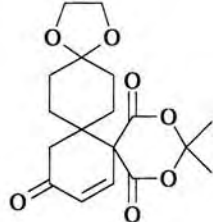
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-2	1. PhC(CN)NMe ₂ Li ⁺ (65) 2. AgNO ₃ , H ₂ O (95) 3. H ₂ O ₂	 (—)	23
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, 25°, 1.5 h	 (61)	434
	A-3	1. PhSeCl, C ₆ H ₆ , 5°, 0.5 h; rt, 0.5 h (75) 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (45)	101
	A-3	1. PhSeCl, <i>n</i> -C ₆ H ₁₄ , (68) 2. H ₂ O ₂ , CH ₂ Cl ₂ , 30°	 (94)	464

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, PhSeCl 2. H ₂ O ₂	 n = 5 (—) n = 6 (—) n = 7 (—) n = 8 (42)	465
	A-2	1. PhSeBr, Et ₃ N, THF, 25° (91) 2. MCPBA, CHCl ₃ , Py, 0°	(93) ^t	96
	A-1	1. LDA, THF, HMPA; PhSeCl 2. O ₃	(37) + (12)	340

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Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc 2. H ₂ O ₂ (30%), THF	(50)	267
	A-1	1. LDA, THF, -78°; PhSeCl 2. NaIO ₄ , NaHCO ₃ , Me ₂ CO, H ₂ O	I, R ¹ = CH ₃ , R ² = H (77)	323
	A-1	1. [Enolate]; Ph ₂ Se ₂ 2. [Ox]	I, R ¹ = CH ₂ =CHCH ₂ , R ² = CH ₃ (30)	466
	A-1	1. LDA; PhSeBr 2. O ₃ , CH ₂ Cl ₂ ; Et ₂ NH, heat	(>73)	50

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Table III.D. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. PhSeO ₂ CCF ₃ 2. [Ox]	(57)	467
	A-2	1. PhSeCl, EtOAc, 20° 2. O ₃ , Et ₂ O, -78°; 20°	(62)	169, 277
	A-1	1. LDA, THF, -70°; PhSeBr 2. H ₂ O ₂ , CH ₂ Cl ₂ , rt, 15 min	(75)	468
	A-1	1. LDA, THF, -70°, 30 min; PhSeBr, -70° to rt 2. H ₂ O ₂ (15%), CH ₂ Cl ₂	I, R = H (75)	469
	—	1. [PhSe] 2. [Ox]	I, R = OC(CH ₃) ₂ OCH ₃ (85) ^k	470

Table III.D. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 30 min; PhSeBr 2. H ₂ O ₂ (10%), CH ₂ Cl ₂ , rt	(60)	471
	A-1	1. LDA, THF, -78°, 10 min; PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, 25°, 1.5 h; NaHSO ₃	(—)	434
	A-1	1. LDA, THF, -70°; PhSeBr 2. H ₂ O ₂ , CH ₂ Cl ₂ , Et ₃ N	(72)	472
	—	NaIO ₄ , THF, H ₂ O, 0° to rt	(30)	473

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-5	1. LDA (0.5 eq), THF, HMPA, -78° to rt 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, heat	(90)	248
	A-1	1. LDA, THF, -78°, 30 min; PhSeBr 2. H ₂ O ₂ (30%), THF, AcOH	(52)	474
	A-1	1. LDA, HMPA (1.3 eq), THF, -78°; PhSeBr (68) 2. NaIO ₄ , MeOH/H ₂ O (10:3), 3 h	(74)	1,2
	A-11	1. PhC(CN)NMe ₂ Li ⁺ ; PhSeBr 2. H ₂ O ₂	(—)	23
	A-11	1. <i>n</i> -Bu ₂ CuLi, THF, 2. TMSCl, Et ₃ N, -20 to 20°; PhSeCl 3. H ₂ O ₂ , AcOH	(63)	245

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA; PhSeCl 2. NaIO ₄ , EtOH	(good)	475
	A-2	1. PhSeCl, EtOAc, 25° 2. H ₂ O ₂	(—) ^f R = MOMO (70)	476 477
	A-1	1. LDA (2 eq), THF, -78°, 20 min; PhSeCl, -78° to rt 2. H ₂ O ₂ (30%), THF, 1 h	(82)	478
	A-1	1. LDA, THF, -78°; PhSeCl, -78° to rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°, 3 h	(80)	479

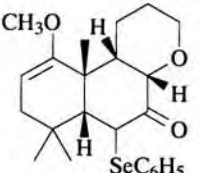
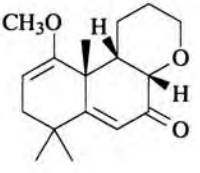
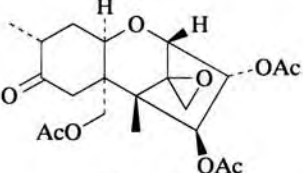
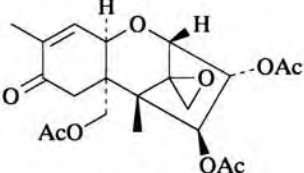
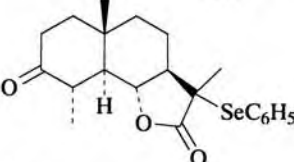
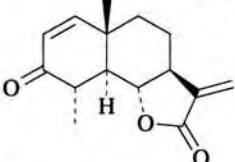
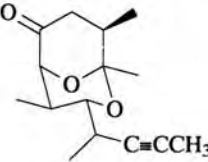
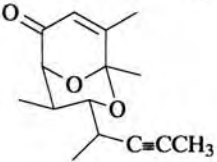
Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-11	1. Me ₂ CuLi, Et ₂ O, -20°; PhSeCl, -20° to rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°, 3 h	 (71)	479
	A-1	1. LDA, THF, -78°; PhthNSePh (90) 2. , CH ₂ Cl ₂	 (68)	480
	A-2	1. PhSeCl, EtOAc, rt 2. H ₂ O ₂ (35%), THF, rt	 (52)	481
	A-1	1. LDA, THF, -78°; PhSeCl, (78) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0 to 25°	 (95)	482

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

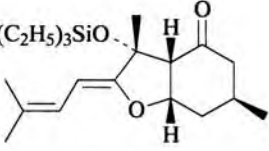
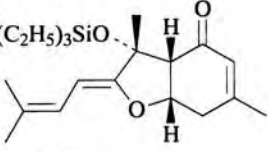
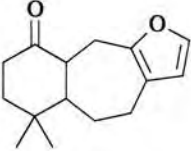
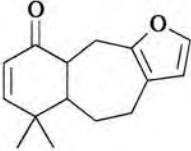
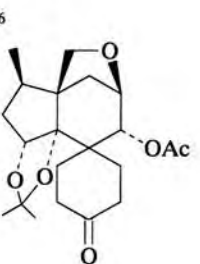
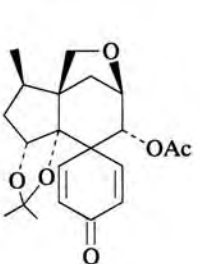
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeBr 2. MCPBA, -78°	 (87)	483
	A-5	1. LDA (0.5 eq), HMPA, THF, -78° to rt (92) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, heat	 (93)	248
	A-2	1. PhSeCl, EtOAc 2. H ₂ O ₂	 (65)	266
	A-1	1. LDA, HMPA, THF, -78°, 1 h; PhSeBr 2. NaIO ₄ , NaHCO ₃ , MeOH, H ₂ O, rt, 3 h	 R ¹ = H, R ² = CH ₃ selenide (75); (69) R ¹ = CH ₃ , R ² = H selenide (82); (46)	484, 485
	A-3	1. PhSeCl, Py, -78° (83) 2. MCPBA, CH ₂ Cl ₂ , -78°; Et ₂ NH, 25°	 (96)	257, 486

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1 ^m	NaIO ₄ , NaHCO ₃ , MeOH, H ₂ O	 (—)	240
	A-2	1. PhSeCl, Py•TsOH, EtOAc, rt (85) 2. O ₃ , CH ₂ Cl ₂ , -78° to rt	 (72)	487
	A-1	1. LDA, THF, -78°; PhSeCl 2. O ₃ , CH ₂ Cl ₂ , -78°; 25°, 1 h	 (60)	488
	A-1	1. LiN(TMS) ₂ , PhSeBr (58) 2. H ₂ O ₂	 (75)	345
	B-2	(PhSeO) ₂ O	" (55)	345

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Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl Isomer A (32) Isomer B (31) 2. Isomer A: NaIO ₄ , MeOH, 2,6-lutidine Isomer B: H ₂ O ₂ , CH ₂ Cl ₂	 (38) (15) ^r	24, 489
	A-1	1. LDA, THF, -70°, 10 min; PhSeBr (80) 2. H ₂ O ₂ (30%), THF, rt, 1.5 h	 (69)	490
	B-2	Ph ₂ Se ₂ , <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (6 eq), Py, PhMe, reflux	 (85)	491

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Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

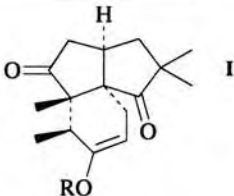
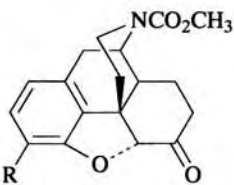
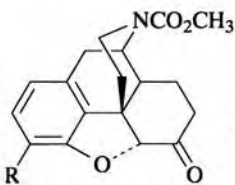
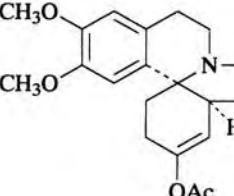
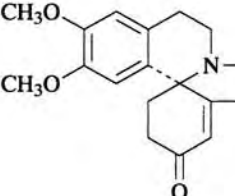
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 I, R = COCH ₃	A-3	1. PhSeCl, AgO ₂ CCF ₃ 2. H ₂ O ₂	II (65)	492
I, R = TMS	A-3	1. PhSeCl, Et ₂ O, -78°, 45 min 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, rt, 2 h	II (50)	492
	A-3	"	II (57) ^k	256, 493
	A-1	1. PhSeCl, HCl, EtOAc 25°, 2 h (86) 2. NaIO ₄ , EtOAc/H ₂ O (7:5), 25°	 R = H (52) R = OCH ₃ (68)	205 191
	A-1	1. MeLi, THF; PhSeCl, -78° 2. NaIO ₄ , H ₂ O, THF	 (64)	189

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

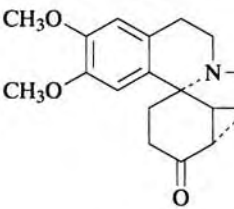
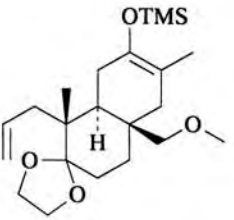
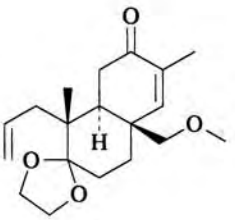
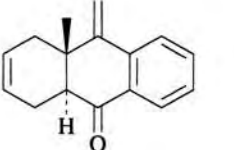
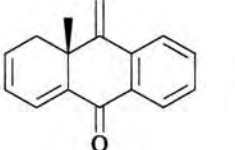
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. Li/NH ₃ , <i>t</i> -BuOH; PhSeCl, (23) 2. NaIO ₄ , THF	" (—)	188
	A-3	1. PhSeCl, C ₆ H ₆ , 0° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	 (80)	251
	A-1	1. LiN(C ₆ H ₁₁) ₂ , THF; PhSeBr (73) 2. NaIO ₄	 (59)	494

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

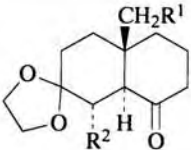
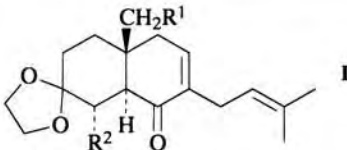
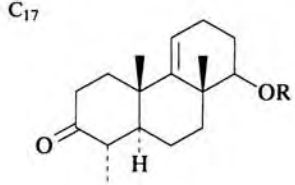
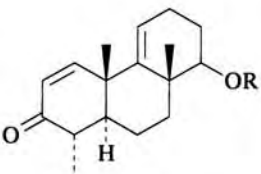
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. LDA, THF, -78°; PhSeCl 2. LDA, THF, HMPA; Me2C=CHCH2Br, 25°, 20 h (83) 3. H2O2 (30%), THF, 0 to 25°, 1 h	 I I, R ¹ = OCH ₃ , R ² = H (65)	51, 495
	D-1	1. LDA, THF, -78°; PhSeCl (85) 2. LDA, THF, HMPA; Me2C=CHCH2Br, -78 to 0° (92) 3. H2O2 (50%), THF, 25°	I, R ¹ = H, R ² = CH ₃ (78)	496
	A-2	1. PhSeCl, EtOAc, 0° to rt 2. MCPBA (2.5 eq), Py, 40°	 R = H (82) R = MOM (27)	497

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

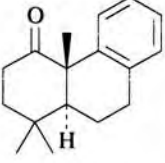
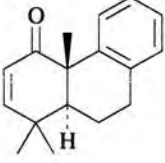
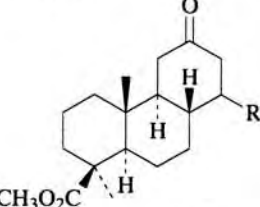
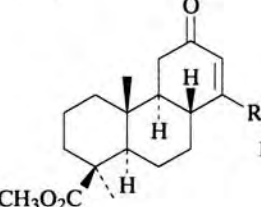
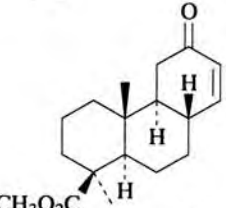
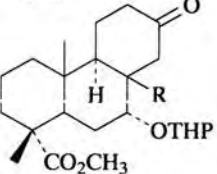
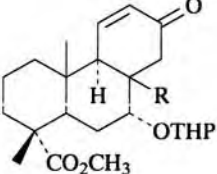
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, -10°; PhSeBr 2. H2O2 (30%)	 (66)	327
	A-2	1. PhSeCl, EtOAc, 25°, 1 h 2. H2O2 (30%), THF, 25°	 I, R = H (>82)	242
	A-11	1. <i>i</i> -Pr ₂ CuLi, Me ₂ S, THF, -78 to -30°, 1 h; PhSeCl (3 eq), -78°, 10 min 2. H2O2 (30%, 10 eq)	I, R = <i>i</i> -C ₃ H ₇ (75)	242, 498
	A-1	1. Ph ₃ CLi, THF, -78°; PhSeBr 2. H2O2 (30%), CH ₂ Cl ₂ , 0° to rt	 I, R = α -H (85)	241

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0° to rt	I, R = β -H (85)	241
	A-2	1. PhSeCl 2. H ₂ O ₂	(66)	499
	A-2	1. PhSeCl, EtOAc, HCl (35) 2. NaIO ₄ , THF, MeOH, H ₂ O	(-)	187
	A-3	1. THMCl, LiI, (TMS) ₂ NH; PhSeCl, THF, Py, -78° 2. MCPBA, CH ₂ Cl ₂	(71)	250, 500

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl 2. MCPBA, CH ₂ Cl ₂ , 0°	R = <i>i</i> -C ₃ H ₇ (50) R = CH ₃ C=CH ₂ (51)	501 501 502
	A-1	1. LDA, THF, -78°; PhSeCl (54) 2. MCPBA, CH ₂ Cl ₂ , rt	I, R = OCH ₃ (92)	346
	A-2	1. PhSeCl, EtOAc, rt, 22 h (80) 2. H ₂ O ₂ (30%), EtOAc, 15°, 3.5 h	I, R = H (86)	259
	A-2	1. PhSeCl 2. H ₂ O ₂ (30%)	R = α -H, I (55) + II (24) + III (15)	273
	A-2	1. PhSeCl, EtOAc (60) 2. PhSeCl, EtOAc 3. H ₂ O ₂ (30%), EtOAc, 10°	R = α -H, III (37) ^o	503

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

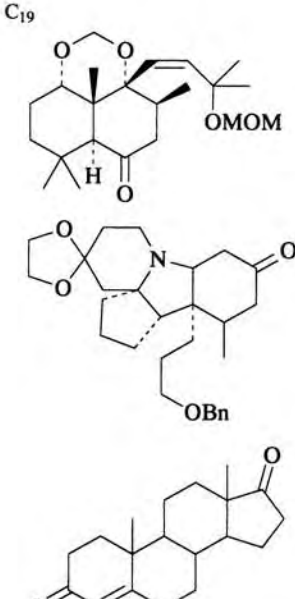
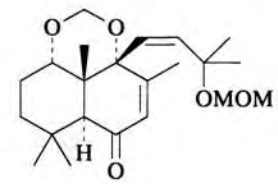
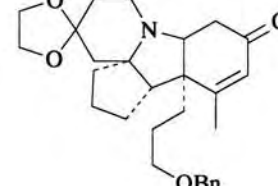
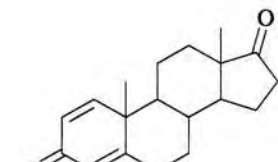
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl 2. H ₂ O ₂ (30%)	R = β -H, I (88) + II (4)	273
	A-1	1. LDA, THF, -78°; PhSeBr 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (81)	504
	A-1	1. LiTMP, THF, -78°; PhSeCl 2. MCPBA, CH ₂ Cl ₂ , -20°	 (59)	185
	B-2	(PhSeO) ₂ O (0.18 eq), PhIO ₂ (3.3 eq), C ₆ H ₆ , reflux 12 h	 (72)	89,92

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

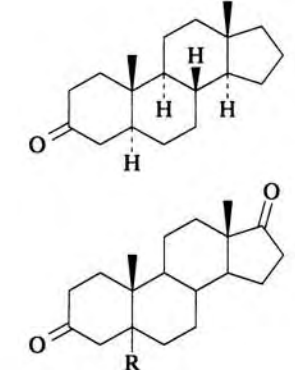
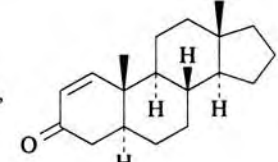
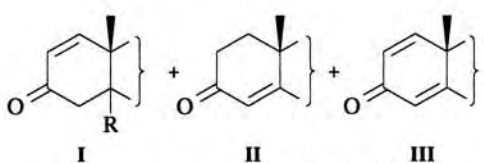
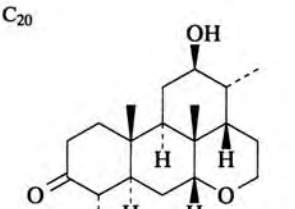
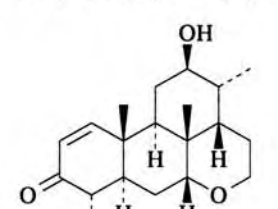
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, DMF, 80 min (56) 2. H ₂ O ₂ (30%), EtOAc/THF (3:1), <34°, 1 h	 (85)	505
	A-2	1. PhSeCl 2. H ₂ O ₂ (30%)	 I II III R = α -H, I (89) + II (2) + III (4) 273 R = β -H, I (16) + II (74) + III (4) 273	
	A-2	1. PhSeCl, TsOH, EtOAc 2. MCPBA, Py	 (>58)	506

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

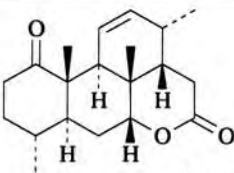
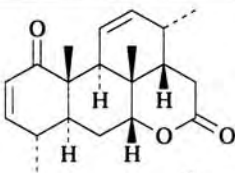
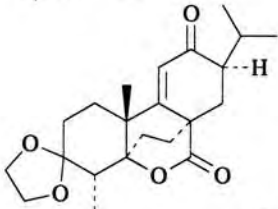
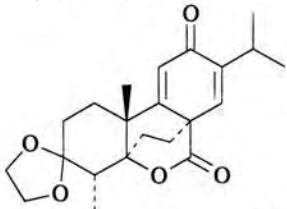
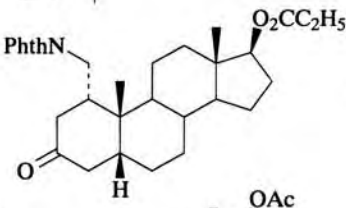
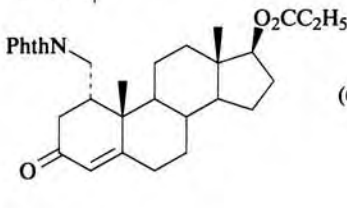
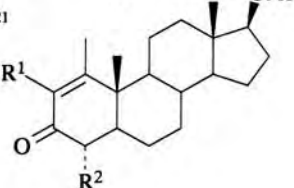
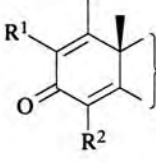
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. TMSI, (TMS) ₂ NH, Et ₃ N 2. PhSeCl, THF, 0° 3. H ₂ O ₂ , Py, 0°	 (82)	255
	A-1	1. LDA, THF, HMPA, -78°, 30 min; PhSeCl, -78°, 90 min 2. H ₂ O ₂ (7%), CH ₂ Cl ₂ , rt, 45 min	 (69)	507
	A-2	1. PhSeCl, EtOAc, 1 h (68) 2. H ₂ O ₂	 (68)	508
	B-2	Ph ₂ Se ₂ , PhIO ₂ , PhMe, 80 to 90°	 R ¹ = H, R ² = CH ₃ (31) R ¹ = CH ₃ , R ² = H (78) R ¹ = R ² = CH ₃ (33)	509

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

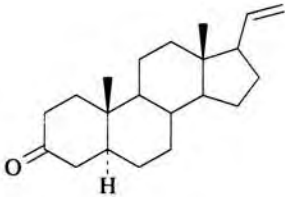
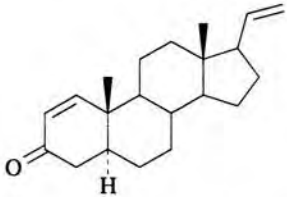
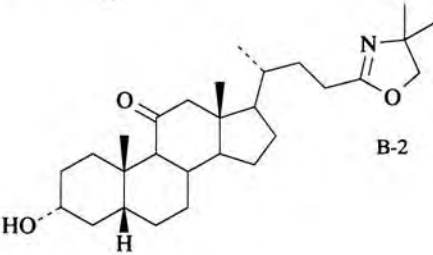
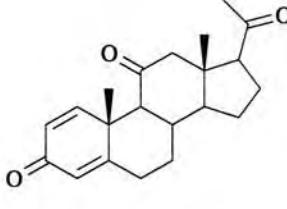
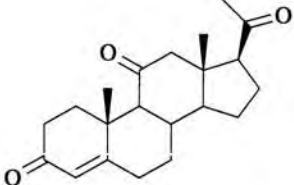
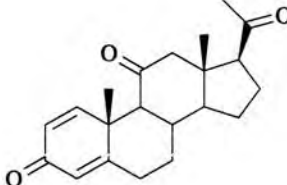
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 1 h; PhSeCl, 30 min 2. NaIO ₄ , MeOH, H ₂ O, EtOAc, 1 h	 (55)	510
	B-2	Ph ₂ Se ₂ , PhIO ₂ , PhMe, reflux	 (12)	90
	B-2	(PhSeO) ₂ O, (0.18 eq), PhIO ₂ (3.3 eq), C ₆ H ₆ , reflux 12 h	 (51)	89,92

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

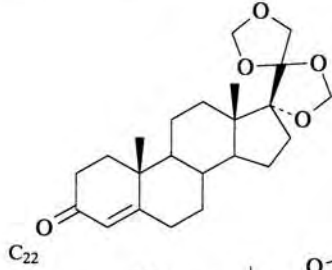
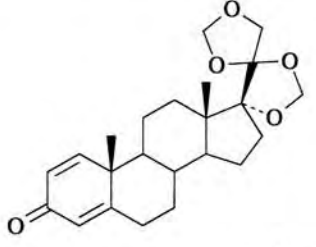
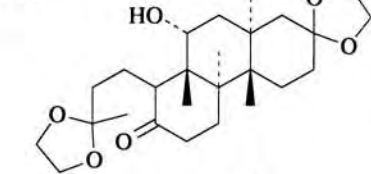
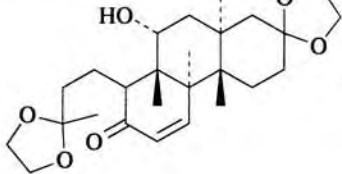
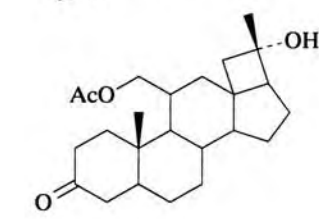
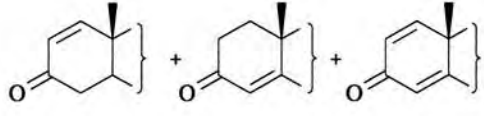
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl 2. H ₂ O ₂	 (—)	265
	A-1	1. LDA (2.16 eq), THF, -78°; PhSeBr 2. H ₂ O ₂ (30%), THF, Py	 (—)	511
	A-1	1. PhSeCl, EtOAc, 25° 2. H ₂ O ₂ (30%), EtOAc, THF, 25°	 I (60) + II (13) + III (12)	512

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

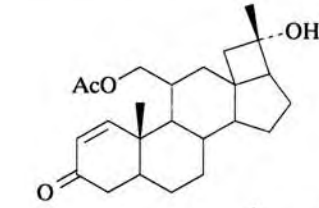
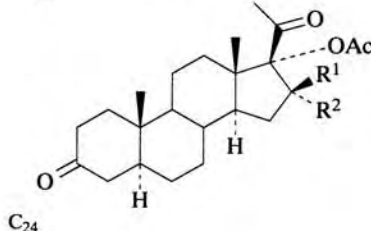
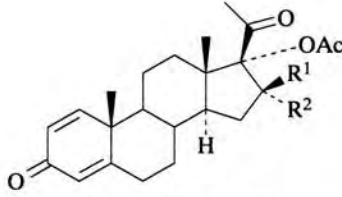
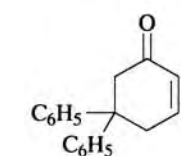
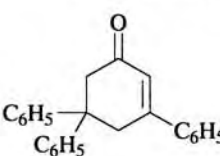
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. PhSeCl, EtOAc, 25° 2. H ₂ O ₂ (30%), EtOAc, THF, 25°	I (47) + II (—) + III (12) ^a	512
	B-2	Ph ₂ Se ₂ (0.2 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (3.2 eq), PhMe, reflux 2.5 h	 R ¹ = CH ₃ , R ² = H (86) R ¹ = H, R ² = CH ₃ (75)	89,92
	A-11	1. Ph ₂ CuLi, THF, -40°; PhSeBr 2. H ₂ O ₂ (30%), Py, CH ₂ Cl ₂	 (82) ^a	513

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

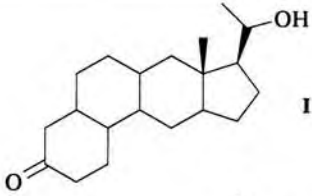
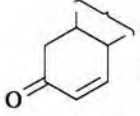
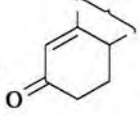
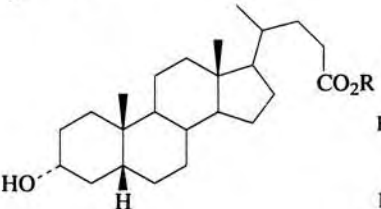
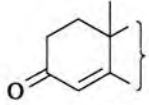
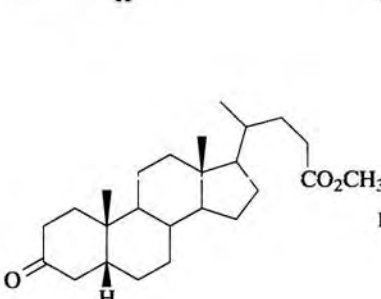
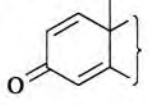
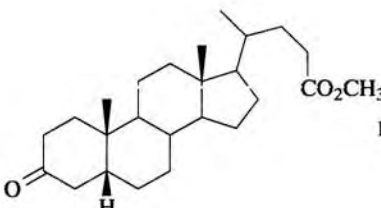
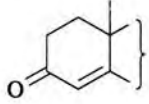
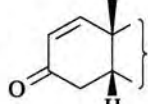
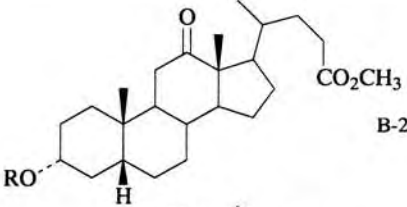
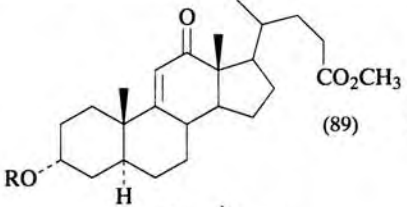
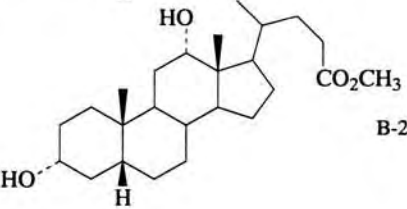
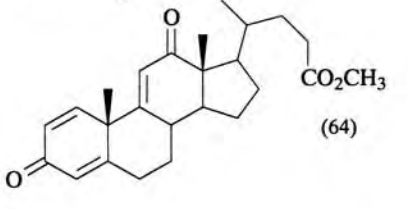
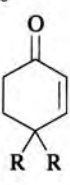
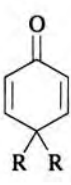
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt, 40 min 2. H ₂ O ₂ (30%), EtOAc, THF, rt	 II +  I:II:III = 19:72:9	514
	B-2	(PhSeO) ₂ O, camphorsulfonic acid, THF, 5°	 R = H (54)	231
	B-2	Ph ₂ Se ₂ (0.2 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (3.3 eq), PhMe, reflux 3 h	 R = CH ₃ (84)	89,92
	B-2	Ph ₂ Se ₂ (0.1 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (2 eq), camphorsulfonic acid, THF, 20°	 (62) +  (10)	231

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	Ph ₂ Se ₂ (0.1 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (5 eq), PhMe, reflux (R = Ac, CHO)	 (89)	89
	B-2	Ph ₂ Se ₂ (0.1 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (7.5 eq), PhMe, reflux	 (64)	89
	A-1	1. LDA, THF, -78°, 1.5 h; PhSeBr, -78° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , rt, 2 h	 (59)	515

R = 1-naphthyl

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

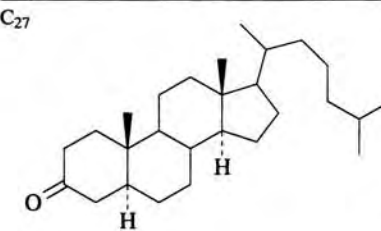
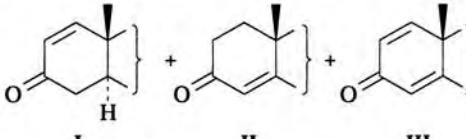
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
				
	A-2	1. PhSeCl, EtOAc, rt 2. H ₂ O ₂ (30%), THF, rt	I (84) + II (3) + III (4) I (58) + II (13) + III (12)	3 512
	B-2	Ph ₂ Se ₂ (0.1 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (2 eq), camphorsulfonic acid	I (70) + II (8.5)	231
	B-2	(PhSeO) ₂ O (2 eq), PhSeCl, 132°, 2 h	III (83)	14
	B-2	(PhSeO) ₂ O (0.2 eq), PhIO ₂ (3.3 eq), C ₆ H ₆ , reflux 24 h	III (84)	92
	B-2	Ph ₂ Se ₂ (0.3 eq), N ₂ O ₃ , PhCl, 110°	III (63)	89
	B-2	Ph ₂ Se ₂ (0.3 eq), PhIO ₂ , PhCl, 110°	III (65)	89
	B-2	(PhSeO) ₂ O (0.2 eq), PhIO ₂ , PhCl	III (84)	89

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

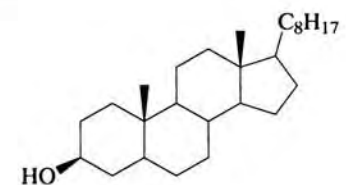
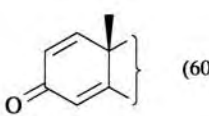
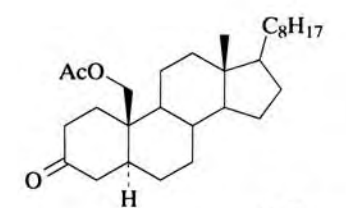
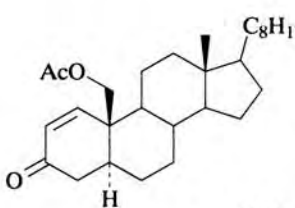
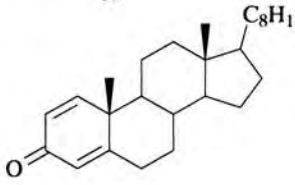
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O (4 eq), PhCl, reflux 20 min	 (60)	282
	B-2	(PhSeO) ₂ O (0.2 eq), PhIO ₄ (3.3 eq), C ₆ H ₆ , reflux 24 h	" (81)	89,92
	B-2	Ph ₂ Se ₂ (0.03 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H (2 eq), PhMe, reflux 16 h	" (73)	89,92
	A-1	1. [PhSe] 2. [Ox]	 (—)	516
	B-2	(PhSeO) ₂ O, PhCl, 95°, 45 min	 (76)	14, 517

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

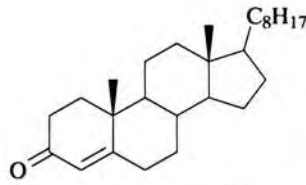
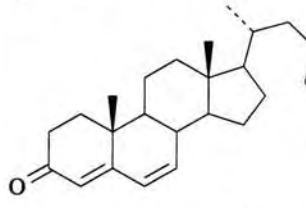
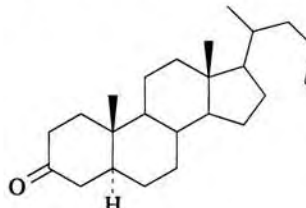
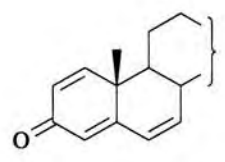
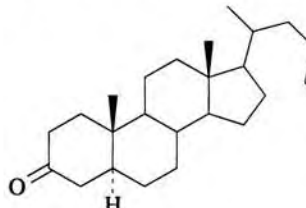
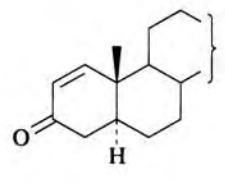
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc 2. H ₂ O ₂	" (89)	512
	B-2	(PhSeO) ₂ O, PhCl, 132°, 40 min	" (92)	14
	B-2	(PhSeO) ₂ O, PhCl, 95°, 1 h	 (50) ^k	14
	B-2	Ph ₂ Se ₂ (0.1 eq), <i>m</i> -O ₂ IC ₆ H ₄ CO ₂ H, camphorsulfonic acid, THF	 (69)	231

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

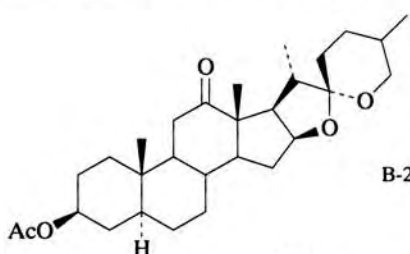
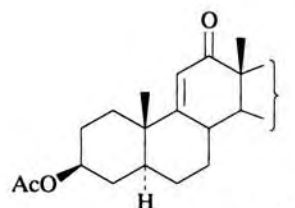
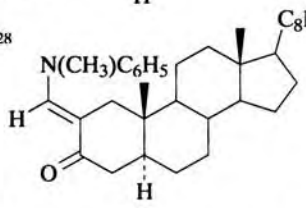
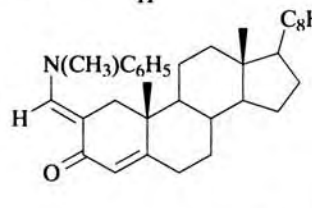
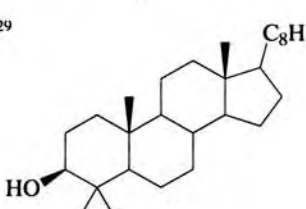
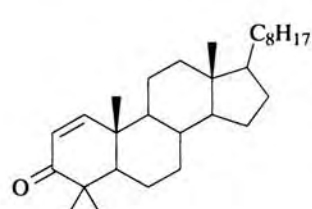
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O (2 eq), PhCl, 132°	 (91)	14
	A-1	1. LDA, THF, -70°; PhSeCl (58) 2. H ₂ O ₂ (30%), THF, Py	 (89)	512
	B-2	(PhSeO) ₂ O (2 eq), PhCl, reflux 12 min	 (65)	282

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

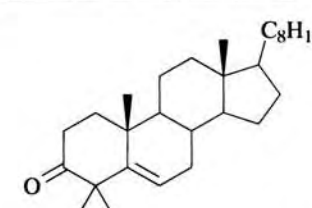
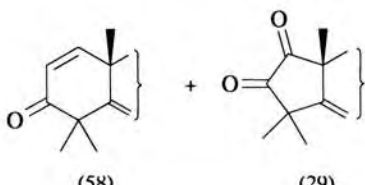
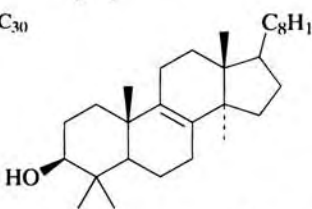
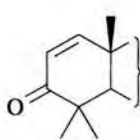
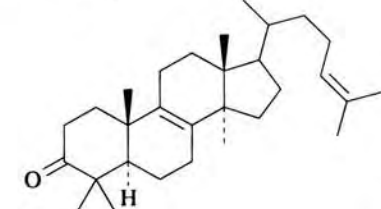
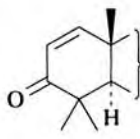
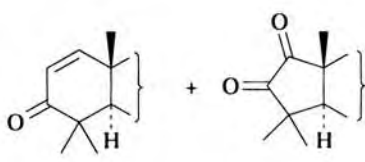
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O (2 eq), PhCl, 100°		14, 517
	B-2	(PhSeO) ₂ O (2 eq), PhCl, reflux 10 min		282
	B-2	(PhSeO) ₂ O, PhCl, 95°, 45 min		14
	B-2	Ph ₂ Se ₂ (0.25 eq), <i>t</i> -BuOOH (5 eq), PhCl, 100°, 25 min		14

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

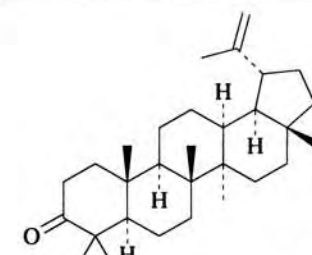
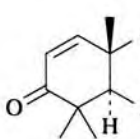
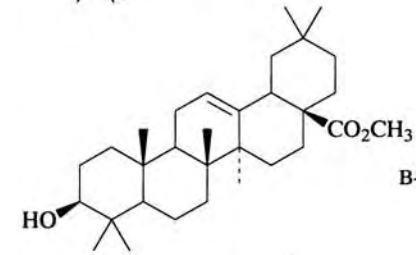
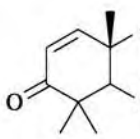
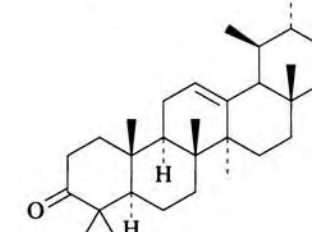
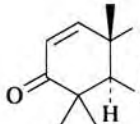
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O, PhCl, 101°, 15 min		14, 517
	B-2	(PhSeO) ₂ O (2 eq), PhCl, reflux 7 min		282
	B-2	(PhSeO) ₂ O, PhCl, 100°, 25 min		14

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

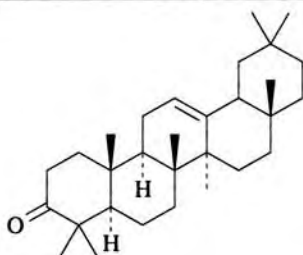
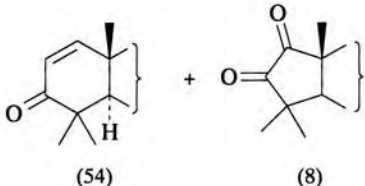
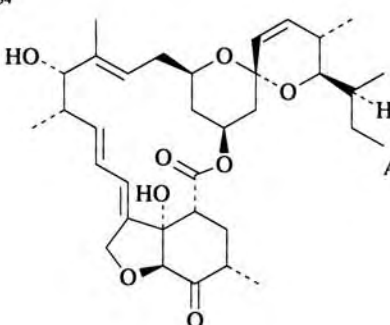
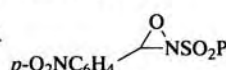
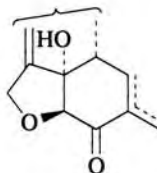
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O, PhCl, 100°, 15 min		14
	A-2	1. TMSOTf, Et ₃ N, CH ₂ Cl ₂ , 0° (93); PhSeCl (90) $\alpha:\beta$ selenides 1:1 2. <i>n</i> -Bu ₄ NF (94) 3. 	 from α -selenide: <i>endo</i> (35) from β -selenide: <i>exo</i> (23)	518

Table IIID. α,β -Unsaturated Cyclohexanones (Continued)

- ^a The α -phenylselenoketone was also formed by methods A-1 (78%) and A-3 (84%).
^b The yield of selenide dichloride was only 65% if sulfonyl chloride was not added.
^c The α -methoxyselenide was prepared by methanolysis of the α -bromoselenide.
^d The ratio of 2-phenylseleno to 6-phenylselenoketones was 87:13.
^e The yield was corrected for recovered starting material.
^f The enone had 26% ee.
^g The ratio of 2-phenylseleno to 6-phenylselenoketones was 2:98.
^h The enone could not be isolated.
ⁱ Oxidation with benzeneseleninic acid failed.
^j Saegusa oxidation gave 60% yield.
^k The yield includes other steps.
^l R was one or more of H, OH, Cl, F, OMOM and was not specified.
^m The enolate was prepared by an anionic oxy-Cope rearrangement.
ⁿ The methyl and phenylseleno groups were *cis* in isomer B.
^o The second treatment with selenenyl chloride produced the α -chloroselenide.
^p The yield was calculated by the authors.
^q The reference experimental gives 1:1 PhLi-CuI, but the text reports "Ph₂CuLi".

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings

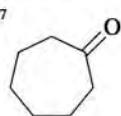
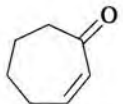
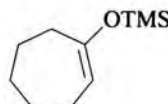
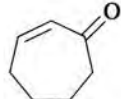
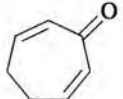
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux	 (55)	2
	A-2	1. 2-PyrSeBr, HCl, EtOH, reflux 0.5 h (84) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux	" (100)	234
	A-1	1. LDA, THF, -72°, 2 h; PhSeCl, THF, -72 to 0° 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	" (90)	350
	B-3	1. PhSeCl ₃ (0.5 eq), Et ₂ O, 0°, 20 min; SO ₂ Cl ₂ (89) 2. NaHCO ₃ , CH ₂ Cl ₂ , H ₂ O	" (74)	72, 382
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (97) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux	" (100)	47
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° (81) ^a 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	 (61)	2

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

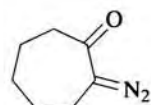
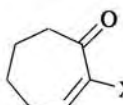
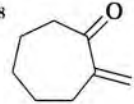
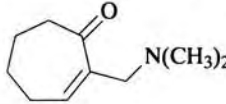
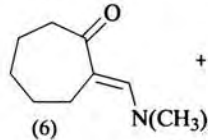
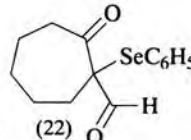
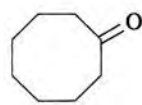
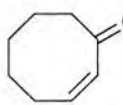
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-9	1. PhSeX, CH ₂ Cl ₂ , rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	 X = Cl (78) X = Br (64) X = OAc (74)	155, 152
	A-10	1. PhSeNMe ₂ , C ₆ H ₆ , 25°, 16 h 2. MCPBA, -50°; -25°, 30 min	 (48) +  (6) +  (22)	41
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78° (70) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux	 (74)	2
	A-2	1. 2-PyrSeBr, HCl, EtOH (59) 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux	" (94)	234
	B-3	1. PhSeCl ₃ , Et ₂ O, 0°; SO ₂ Cl ₂ (98) 2. NaHCO ₃ , CH ₂ Cl ₂ , H ₂ O	" (80)	72, 382

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

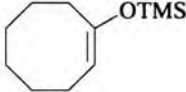
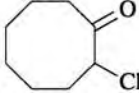
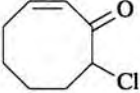
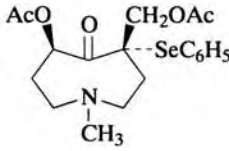
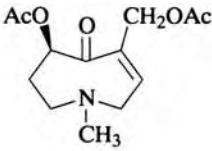
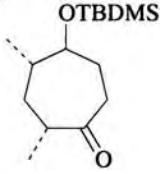
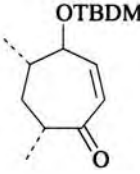
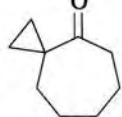
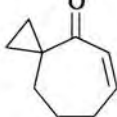
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h (88) ^b 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH, CCl ₄ , reflux 0.5 h	" (94)	47
	A-2	1. PhSeCl, CH ₂ Cl ₂ , rt, 24 h (54) 2. SO ₂ Cl ₂ ; NaHCO ₃ , H ₂ O, CH ₂ Cl ₂	 (60)	72
	—	H ₂ O ₂ (30%), AcOH, rt, 2 h	 (53)	519
	A-1	1. LTMP, THF, -78°, 25 min; PhSeCl, -78°, 30 min; 0°, 1 h 2. H ₂ O ₂ (30%), THF, AcOH, 0 to 25°	 (57)	520
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, -78°, (85) 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (85)	2

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

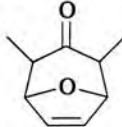
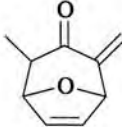
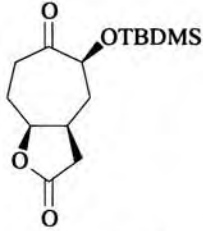
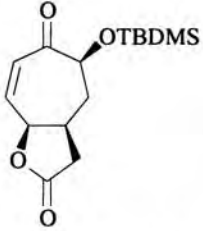
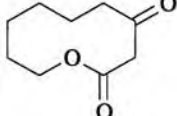
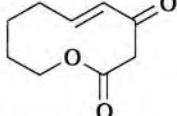
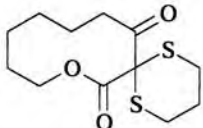
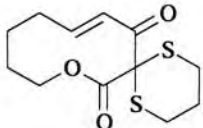
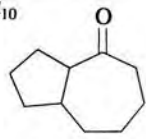
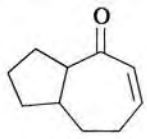
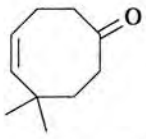
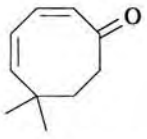
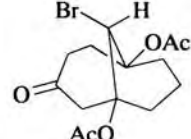
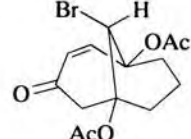
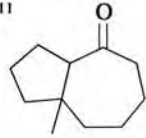
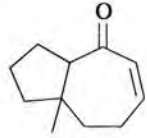
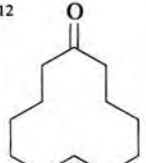
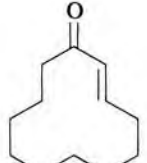
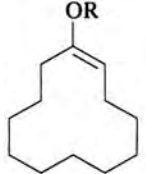
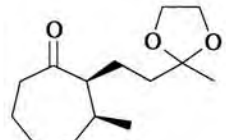
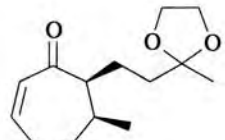
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 40 min; PhSeCl, 1 h, (73) 2. H ₂ O ₂ (30%), THF, 0°, 1 h	 (80)	521
	A-2	1. PhSeCl, H ⁺ 2. H ₂ O ₂	 (40)	269
	A-1	1. LDA (2.5 eq), THF, HMPA, 0°, 25 min; PhSeBr, (1.3 eq) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0 to 25°	 (14) ^c	522, 523
	A-1	1. LDA, THF, -78°, 1 h; PhSeBr, 0° 2. H ₂ O ₂ (30%), THF, AcOH, 0°	 (50)	40

Table IIIE. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	A-1	1. LDA, THF, -72°, 15 min; PhSeCl, THF, -78° to rt, 2 h, (86) 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (84)	350
	A-1	1. LDA, THF, -78°; PhSeCl (39, 5:1 mixture of regioisomers) 2. H ₂ O ₂ (14%), CH ₂ Cl ₂ , Py, 15° to rt	 (45)	524
	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, 0° to rt, 10 h	 (60)	525
C ₁₁ 	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, (82) 2. O ₃ , CH ₂ Cl ₂ , -78°; <i>i</i> -Pr ₂ NH, CCl ₄ , reflux	 (71)	526
C ₁₂ 	A-1	1. LDA, THF, -78°, 10 min; PhSeBr, -78 to 0° 2. H ₂ O ₂ (30%), AcOH, <25°	 (72)	2,1

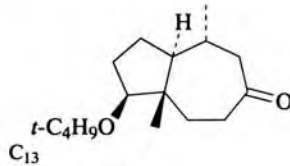
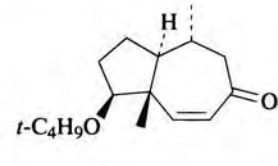
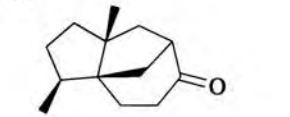
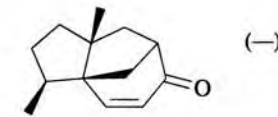
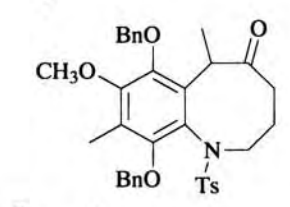
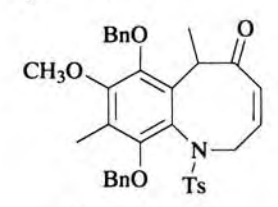
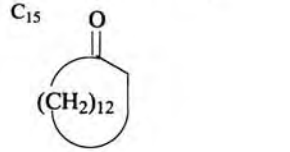
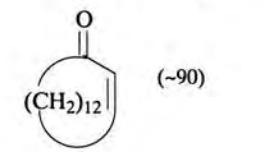
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Table IIIE. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, EtOAc, rt, 5 h 2. H ₂ O ₂ (30%), THF, rt, 1 h or 2. CH ₃ CO ₃ H	" (77)	3
	B-3	1. PhSeCl ₃ (0.5 eq), Et ₂ O, 0°, 20 min; SO ₂ Cl ₂ (98) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (79)	72, 382
	B-2	Ph ₂ Se ₂ , oxidizing Pt electrode (11.9 F/mol), MgSO ₄ , MeCN/H ₂ O (5:2), 66-68°	" R = Ac (81)	238
	A-3	1. 2-PyrSeBr, CH ₂ Cl ₂ , rt, 0.5 h, (100) ^d 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₂ NH; CCl ₄ , reflux	" R = TMS (82)	47
	A-1	1. LiTMP, THF, -78°; PhSeBr, 0° 2. H ₂ O ₂ (30%), EtOAc, 0 to 25°	 (55)	527

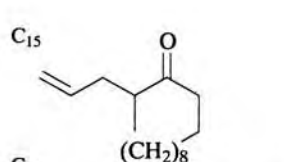
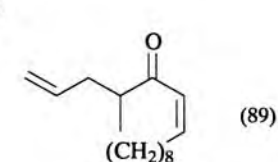
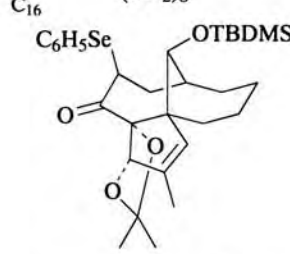
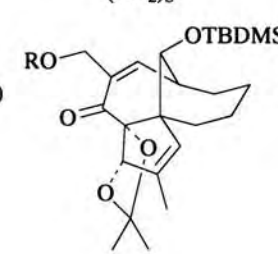
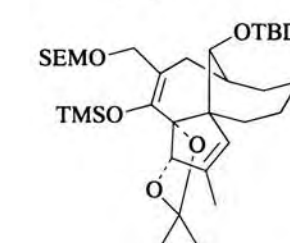
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Table IIIE. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; PhSeBr 2. H ₂ O ₂ , THF	 (81)	528
	A-1	1. LDA; PhSeBr 2. [Ox]	 (—)	529
	A-2	1. PhSeCl (1.5 eq), HCl, EtOAc 2. NaIO ₄ , H ₂ O, THF, rt, 16 h	 (67)	530
	A-1	1. LDA, THF, -78°, 55 min; PhSeCl 2. H ₂ O ₂ (30%), THF, AcOH, 0° to rt	 (~90)	531
	A-2	1. PhSeCl, EtOAc, rt 2. H ₂ O ₂ (30%)	" (60)	531

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Table IIIE. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-3	1. PhSeCl ₃ (0.5 eq), Et ₂ O, 0°, 20 min; SO ₂ Cl ₂ (90) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	" (92)	72
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂ (30%)	 (89)	532
	D-1	1. CH ₂ O, KOH, MeOH, H ₂ O (80) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0 to 25°, 1.25 h	 I, R = H (46) ^e	102, 533
	A-3	1. PhSeCl, THF, <i>t</i> -Bu ₂ Py, 48 h 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0° to rt, 40 min	" I, R = SEM (31)	102

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Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

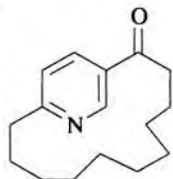
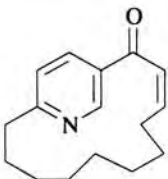
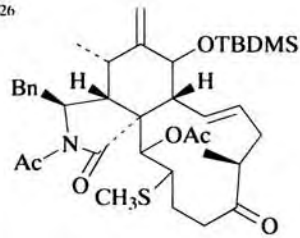
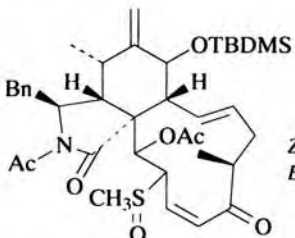
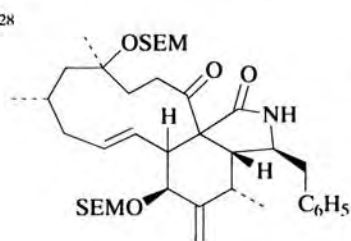
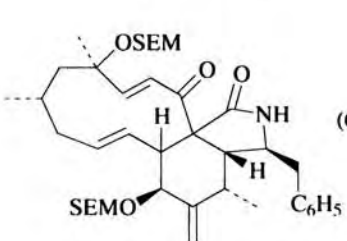
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78° , 15 min; PhSeCl; rt, 2 h 2. H_2O_2 (30%), CH_2Cl_2 , Py, 25° , 2 h	 (40)	534
	A-3	1. TMSCl, DBU, MeCN, PhSeSe(Me)Ph $^+BF_4^-$, CH_2Cl_2 , -78° (93) 2. MCPBA, $NaHCO_3$, CH_2Cl_2 , -78 to -20°		Z enone (66) 535 E enone (20)
	A-3	1. LDA, TMSCl 2. <i>n</i> -Bu $_2$ NF, PhSeCl (>21) 3. H_2O_2 , Py,	 (65)	103

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (Continued)

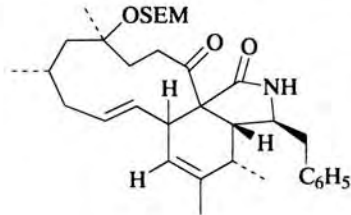
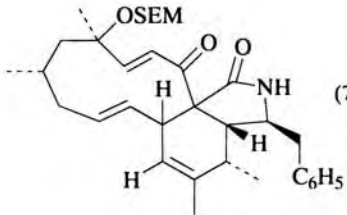
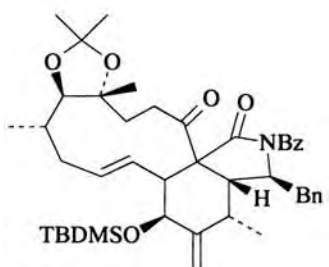
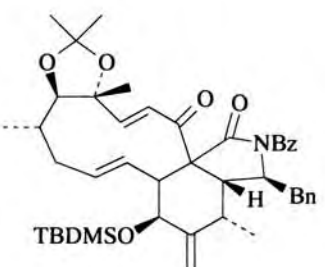
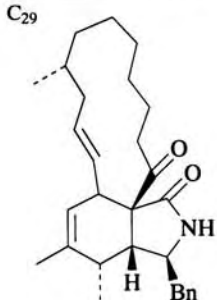
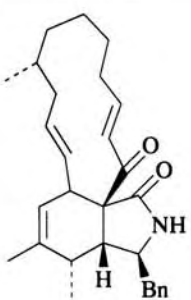
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. LDA, TMSCl 2. <i>n</i> -Bu $_4$ NF, PhSeCl (>78) 3. H_2O_2 , Py	 (75)	103
	A-1	1. LDA, PhSeCl (70) 2. KOH, MeOH (85) 3. H_2O_2 , Py	 (67)	162

Table III.E. α,β -Unsaturated Cycloheptanones and Larger Rings (*Continued*)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 C ₂₉	A-1	1. LDA, THF, -78°; PhSeCl (62) 2. H ₂ O ₂ , Py, CH ₂ Cl ₂ , rt, 2 h	 (65)	536

^a The α -selenoketone was also formed by methods A-1 (79%) and A-2 (84%).

^b The α -selenoketone was also formed by methods A-1 (61%) and A-2 (59%).

^c The yield was calculated by the present authors.

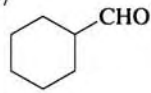
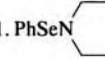
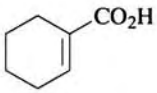
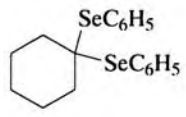
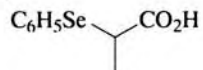
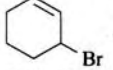
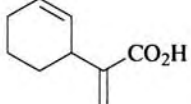
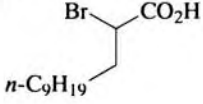
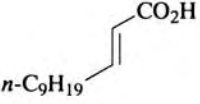
^d The α -selenoketone was also formed by methods A-1 (79%) and A-2 (61%).

^e Other oxidants (NaIO₄, MCPBA, *t*-BuOOH) were less effective.

Table IV. α,β -Unsaturated Acids

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₃ 	A-2	1. PhSeN O, CH ₂ Cl ₂ , 20° 2. H ₂ O ₂ (30%), THF, -10 to 20°	 R = H (50) R = CH ₃ (50) R = C ₂ H ₅ (63) R = <i>n</i> -C ₃ H ₇ (65) R = C ₆ H ₅ (97) R = C ₆ H ₁₁ (70)	236
C ₄ 	A-2	1. PhSeN O, CH ₂ Cl ₂ , 20° 2. H ₂ O ₂ (30%), THF, -10 to 20°	 R = CH ₃ (74) R = C ₂ H ₅ (62) ^a R = <i>n</i> -C ₃ H ₇ (61) ^a R = C ₆ H ₅ (65) R = C ₆ H ₁₁ (55) ^a	236
C ₅ 	A-2	1. PhSeN O, CH ₂ Cl ₂ , 20° 2. H ₂ O ₂ (30%), THF, -10 to 20°	 R = CH ₃ (57) R = C ₆ H ₅ (75) <i>E:Z</i> = 55:45 R = (CH ₂) ₃ C ₄ H ₉ - <i>t</i> (92)	236
	A-1	H ₂ O ₂ (30%), THF, 0°	 (quant)	537

Table IV. α,β -Unsaturated Acids (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₇ 	A-2	1. PhSeN  O, CH ₂ Cl ₂ , 20° 2. H ₂ O ₂ (30%), THF, -10 to 20°	 (80)	236
	D-3	1. <i>n</i> -BuLi, THF, -78°; CO ₂ 2. H ₂ O ₂ , THF, 0°	" (60)	16
C ₉ 	D-1	1. LDA (2.2 eq), THF, 0 to 40°;  , 25°, 2 h (82) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 30 min	 (90)	53
C ₁₂ 	C-1	1. PhSe ⁻ , KOH, EtOH, 25° 2. H ₂ O ₂ , THF, AcOH, 0 to 25°	 (91)	199

^a Other regioisomers were not reported.

Table V. α,β -Unsaturated Carboxylic Esters

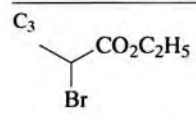
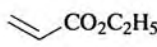
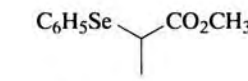
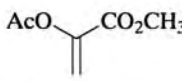
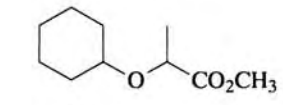
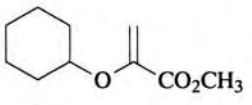
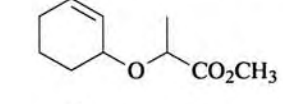
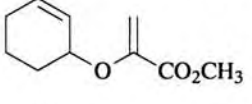
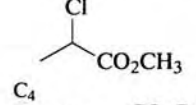
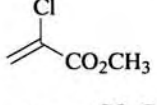

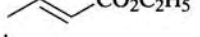
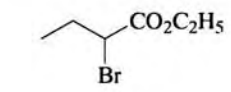
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	C-1	1. Polymer-PhSeNa, EtOH 2. H ₂ O ₂ (30%), EtOH, 30°	 (98)	431
	G-1	1. MCPBA, THF, -22°; Ac ₂ O, THF, Py, -20 to 0° (32) 2. H ₂ O ₂ (30%), EtOAc, 0°, 2 h	 (44)	158
	A-1	1. LDA, THF, -70°, 1 h; PhSeBr, -70° 2. H ₂ O ₂ (30%), EtOAc, 0°, 2 h	 (30)	158
	A-1	1. LDA, THF, HMPA, 70°, 1 h; Ph ₂ Se ₂ , -70°, 1 h; -40°, 3 h 2. H ₂ O ₂ (30%), EtOAc, 0°, 2 h	 (36)	158
	A-1	1. LDA, THF, -78°, 1 h; PhSeBr, -70° to rt, 1 h (69) 2. H ₂ O ₂ (30%), EtOAc, 0°, 2 h	 (—)	158
	A-1	1. LCA, THF, -78°, 5 min; PhSeBr, -78° to rt 2. CH ₃ CO ₃ H (40%), EtOAc, 25°, 2 h	 (83)	3
	C-1	1. Polymer-PhSeNa, EtOH 2. H ₂ O ₂ (30%), EtOH	" (75)	538
	C-1	1. PhSeNa, EtOH, 25° 2. CH ₃ CO ₃ H, EtOAc, 25°, or H ₂ O ₂	" (89)	3

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. LCA, THF; EtBr 2. CH3CO3H, EtOAc, 25°, or H2O2	" (65)	3
	—	H2O2 (30%), EtOAc, 0° to rt	I	539
	A-1	1. LTMP (2 eq), THF, -78°; PhSeCl 2. H2O2 (30%), CH2Cl2, Py, rt, 15 min	I, R ¹ = OTBDMS, R ² = N(CH2CH=CH2)Boc (48)	540
	A-1	1. LiN(TMS)2, THF, TMEDA, -78°, 30 min; PhSeCl 2. H2O2 (30%), Me2CO, 0° to rt	I, R ¹ = F, R ² = NHCO2Bn (76)	541
	D-1	MCPBA, CH2Cl2, -10°; <i>i</i> -Pr2NH, CCl4, reflux	(55)	542
	A-1	1. LDA, THF, -78°, 15 min; Ph2Se2, THF, -78° (56) 2. H2O2 (15%), CH2Cl2, Py, rt	(32)	178

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 15 min; Ph2Se2, -78°, 5 min (65) 2. NaIO4, NaHCO3, H2O/MeOH (0.75:4.5), rt overnight	(69)	178
	A-1	1. LiN(TMS)2, THF, -76°; PhSeBr 2. MCPBA, EtOAc, 0° to rt	(76) R = H (—) R = C6H5 (—)	112
	A-1	1. Base, PhSeCl (56) 2. SO2Cl2; NaHCO3, CH2Cl2	(76)	72
	A-1	1. LDA, PhSeCl 2. H2O2	(—)	543
	A-1	1. LDA, THF, -78°; PhSeBr, -78 to 0° 2. H2O2 (30%), THF, AcOH, rt	(96)	2,217

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-3	1. <i>n</i> -BuLi, THF, -78°; MeOCOCI 2. H ₂ O ₂ , THF, 0°	R = C ₆ H ₅ (90) R = CH ₃ (40)	16
	A-1	1. LCA, THF, -78°, 30 min; Ph ₂ Se ₂ , -78 to 25°, 2 h 2. H ₂ O ₂ (30%), 0 to 25°, 1.5 h	(82)	111
	A-1	1. LDA, THF, -78°, 20 min; PhSeBr, -78° 2. H ₂ O ₂ (30%, xs), 0°, 40 min; rt, 1 h	(62)	355
	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, HMPA, -78°, 2 h; -20° to rt 2. NaIO ₄ , MeOH, H ₂ O	I I, R = (CH ₂) ₂ CH=CH ₂ (—)	544
	A-1	1. LDA, THF, -78°, 20 min; PhSeBr 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°	I, R = (CH ₂) ₂ CH(OTBDMS)CH ₃ (74)	545

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂	(58)	546
	A-1	1. LDA, PhSeCl 2. H ₂ O ₂	(—)	184
	A-1	1. LDA, THF, -78°, 1 h; PhSeCl, THF, -78°, 3 h (57) 2. H ₂ O ₂ (27%), AcOH, 0°, 1 h; rt, 12 h	" (60)	547
	A-1	1. LDA (2.4 eq), THF; PhSeCl (36) 2. MCPBA, CH ₂ Cl ₂ , -78 to 20°, 14 h	" (60-64)	548
	A-1	1. LCA, THF, -78°; PhSeBr (47) 2. NaIO ₄ , MeOH, H ₂ O	I, R ¹ = THPO(CH ₂) ₅ (81) R ² = CH ₃	549
	—	1. [PhSe] 2. [Ox]	I, R ¹ = CH ₂ =CH(CH ₂) ₅ (—) R ² = CH ₃	550

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

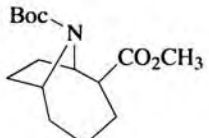
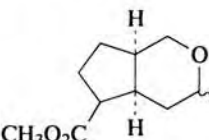
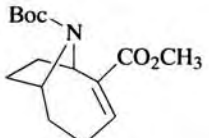
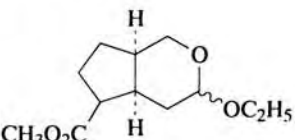
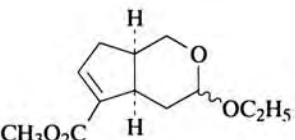
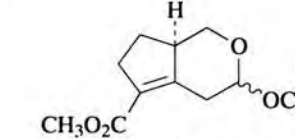
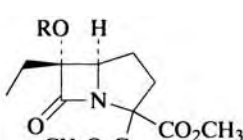
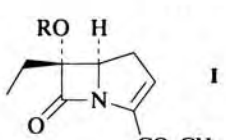
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-1	LDA, THF, -78°; PhSe(O)Cl, -78 to 25°	" (68)	2
	A-1	1. LDA, THF, -78°; PhSeBr/PhSe ₂ , (10:1) (85) 2. MCPBA, CH ₂ Cl ₂ , 0° to rt	 (74)	555
	A-1	1. LDA, THF, -78 to 30°; Ph ₂ Se ₂ , -78° (93) 2. MCPBA, CH ₂ Cl ₂ , -40°; Et ₃ N, rt, 1 h	 I +  II (98) I:II = 6:1	42
	A-8	NaI (2 eq), Ph ₂ Se ₂ , HMPA, 80°, 2 h R = CH ₃ (51); R = THP (61)	 I R = CH ₃ (76) R = THP (80)	363

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

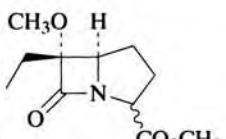
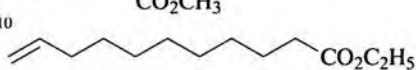
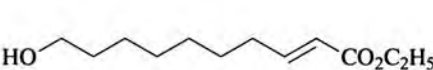
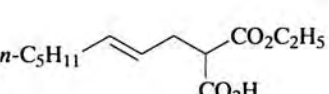
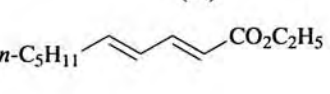
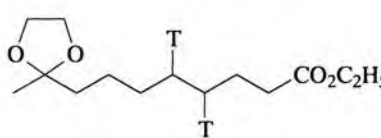
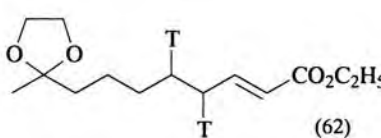
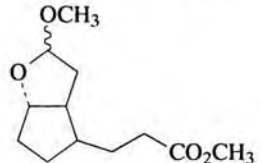
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA (5 eq), THF, -70 to -30°; PhSeCl, -30° 2. MCPBA, CH ₂ Cl ₂ , -30°	I, R = CH ₃ (76)	363
	A-1	1. LDA, THF, -78°; PhSeBr 2. O ₃ , CH ₂ Cl ₂ , -78° 3. NaBH ₄	 (46)	555a
	A-7	1. NaH, PhMe, Ph ₂ Se ₂ , reflux 5 h (74) 2. NaIO ₄	 (91)	555b
	A-1	1. LCA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), THF, AcOH	 (62)	556
	A-1	1. LDA, THF, -78°; PhSeBr 2. [Ox]	(-)	557

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-3	1. $\text{LiN}(\text{C}_6\text{H}_{11})_2$, THF, -78° ; TMSCl; PhSeCl (50) 2. MCPBA, CH_2Cl_2 , -10° ; <i>i</i> -Pr ₂ NH, reflux	(83)	289
	A-2	1. $\text{LiN}(\text{C}_6\text{H}_{11})_2$, THF, -78° ; TMSCl; PhSeCl (only β -selenide) 2. MCPBA, CH_2Cl_2 , -10° ; <i>i</i> -Pr ₂ NH, reflux	(—)	289
	A-2	" ($\alpha:\beta$ selenides 1:1)	α , (—) β , (84) α , (major) β , (—)	289
	A-1	1. LDA, THF, -78° , 10 min; PhSeBr, -78 to 0° 2. AcOH; H_2O_2 (30%), rt	(79) <i>E:Z</i> = 46:54	2,1

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78° ; Ph_2Se_2 , (67) 2. H_2O_2 (30%), CH_2Cl_2 , 0°	(93)	558
	A-1	1. LDA, THF, -78° ; Ph_2Se_2 , HMPA, 30 min; -40° , 1 h 2. H_2O_2 (15%), CH_2Cl_2 , 0° to rt, 1 h	(40)	559
	A-1	1. LDA, THF; Ph_2Se_2 , (81) 2. H_2O_2 , CH_2Cl_2 , H_2O	(69)	560
	A-1	1. $\text{LiN}(\text{TMS})_2$, THF; PhSeBr 2. MCPBA, EtOAc	(—) <i>E:Z</i> = 3:1	112

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. KH, Ph ₂ Se ₂ , THF, 0°; 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°	 (74)	560a
	A-1	1. LCA, THF, -78°; PhSeBr, -78 to 25° 2. CH ₃ CO ₃ H (40%), EtOAc, 25°, 1 h	 (79)	3
	C-1	1. PhSeNa, EtOH, 25° 2. CH ₃ CO ₃ H, EtOAc, 25° or H ₂ O ₂	" (82)	3
	D-1	H ₂ O ₂ (35%) CH ₂ Cl ₂ , -5 to 0°	 (90)	561
	A-1	LDA, THF, -78°; 30 min; PhSeCl, -78° to rt, overnight (76)	 (76) E:Z = 1:1	562, 563

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 30 min; PhSeBr, -78 to 0° 2. H ₂ O ₂ (35%), THF, AcOH, 0° to rt	 (76)	564
	A-1	1. LDA, THF, -78°, 20 min; Ph ₂ Se ₂ , THF, -78 to 20°, 2 h 2. NaIO ₄ , THF, MeOH, H ₂ O, 20°, 30 min	 (71)	565, 566
	A-1	1. KH, THF/DMF (9:1); Ph ₂ Se ₂ , 20°, 0.4 h 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0°	 (>50)	120
	A-1	1. LDA, Ph ₂ Se ₂ , THF (89) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	 I, R ¹ = R ² = H (72)	567, 568

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

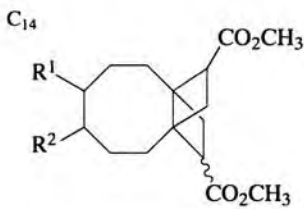
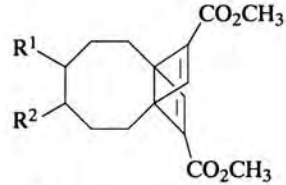
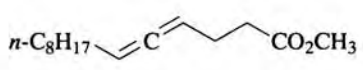
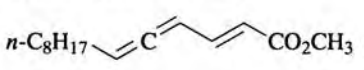
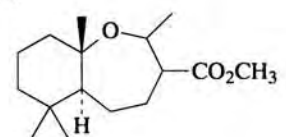
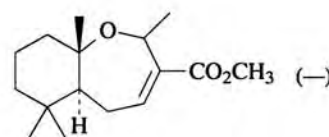
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. [RSe] 2. H ₂ O ₂ , Py	I, R ¹ = R ² = OH (52)	569
	A-1	1. LDA, Ph ₂ Se ₂ , THF, -78° 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0°	I, R ¹ , R ² = double bond (48)	570
	A-1	1. LDA, THF, HMPA, -78°; Ph ₂ Se ₂ (85) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂	I, R ¹ , R ² = double bond (—)	571
C ₁₄ 	A-1	1. LDA (4 eq), THF, -78°; Ph ₂ Se ₂ , HMPA, rt (32) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, rt	 R ¹ = R ² = H (73) R ¹ , R ² = double bond (54)	572 571
	A-1	1. LDA, THF, -78°, 0.5 h; Ph ₂ Se ₂ , -78° 2. NaIO ₄ , H ₂ O, THF, 25°, 10 h	 (88)	574, 573, 175
C ₁₅ 	A-1	1. [PhSe] 2. [Ox]	 (—)	575

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

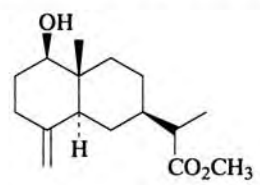
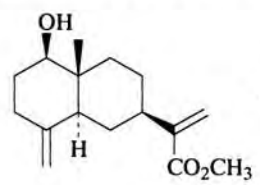
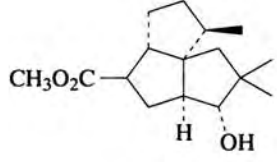
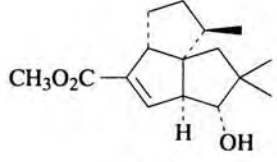
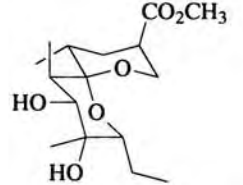
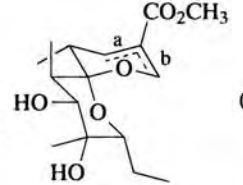
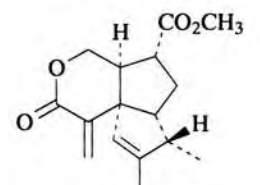
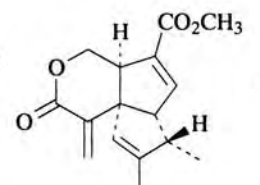
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, Ph ₂ Se ₂ , THF, HMPA, -78 to -40° 2. H ₂ O ₂ , AcOH, THF, 0°, 1 h	 (82)	576
	A-1	1. LDA, PhSeCl, THF, -78 to -30° 2. H ₂ O ₂ (30%), AcOH, THF, 0°	 (75)	577
	A-1	1. LCA, PhSeBr, (MeOCH ₂) ₂ , -78°, 90 min (89) 2. H ₂ O ₂ , Py, CH ₂ Cl ₂ , 25°, 30 min; 45°, 30 min	 (86) a:b = 1:1	44
	A-1	1. LDA (3 eq), THF, -78°, 30 min; PhSeCl, 30 min (47) 2. NaIO ₄ , MeOH, H ₂ O, 30 min	 (97)	578, 579

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

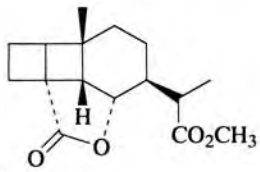
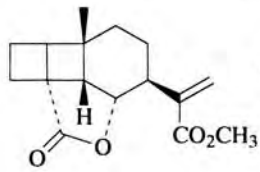
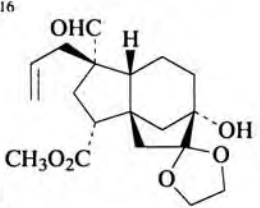
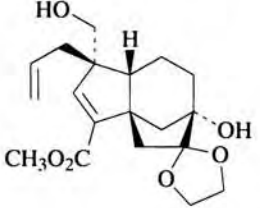
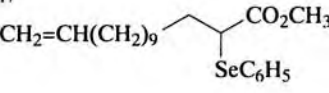
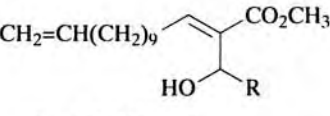
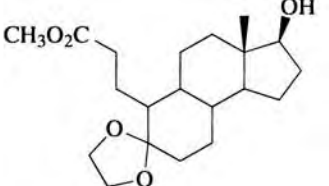
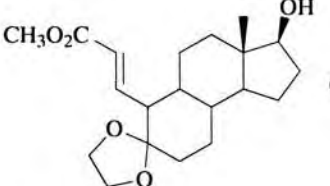
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeBr, 0° 2. H ₂ O ₂ (30%), AcOH	 (33)	580
	A-1	1. KH, Ph ₂ Se ₂ 2. NaBH ₄ 3. H ₂ O ₂ , Et ₂ O, 2,6-lutidine, 20°	 (85)	581
	D-1	1. LDA, THF, -78°; RCHO, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH 0°, 30 min; 25°, 1 h	 R = CH=CH ₂ (—) R = C=CH (>23) E:Z = 3.6:1	291
	—	1. [RSe] 2. [Ox]	 (>60)	582

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

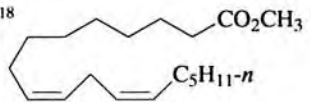
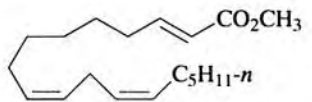
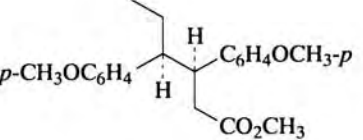
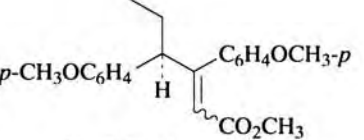
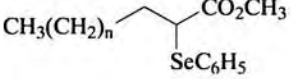
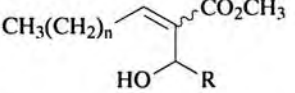
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -70°; PhSeBr, -70° to rt 2. NaIO ₄ , MeOH, H ₂ O, reflux	 (80)	583
	A-1	1. LCA, THF, -78°, 5 min; 25°; Ph ₂ Se ₂ , -78 to 25°, 2 h 2. NaIO ₄ , THF, MeOH, H ₂ O	" (80)	3
	A-1	1. LDA, THF, -78°, 15 min; PhSeBr, THF, -78°; rt 2. H ₂ O ₂ (30%), THF, AcOH, 0 to 25°	 (90) E:Z = 1:1	584
	D-1	1. LDA, THF, -78°; RCHO 2. H ₂ O ₂ (30%, 10 eq), THF, AcOH, 0°, 30 min; 25°, 1-2 h	 R = CH=CH ₂ , n = 14, E:Z = 3.7:1 (>28) R = CH=CH ₂ , n = 12, E:Z = 3.9:1 (>54) R = C=CH, n = 14, E:Z = 4.25:1 (>42) R = C=CH, n = 12, E:Z = 4.1:1 (>51)	291

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

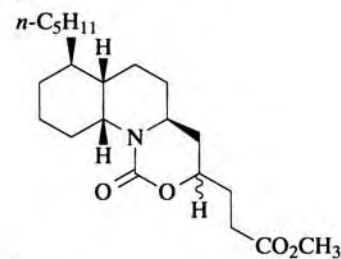
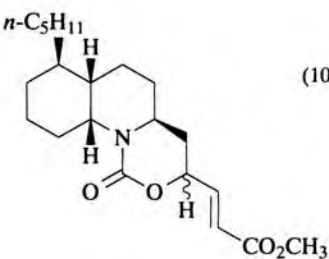
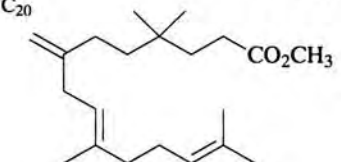
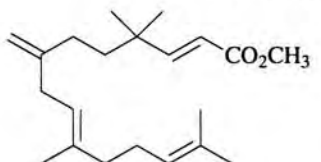
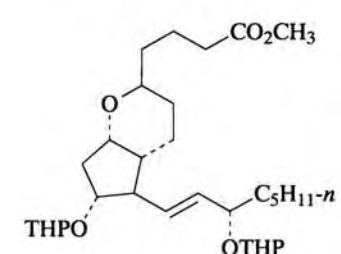
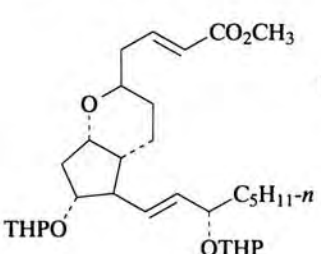
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. [PhSe] 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°	 (100)	586, 585
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0° to rt	 (44)	587
	A-1	1. LDA, THF, -78°, 90 min; Ph ₂ Se ₂ , -78° to rt (46) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , rt, 2 h	 (>61)	588

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

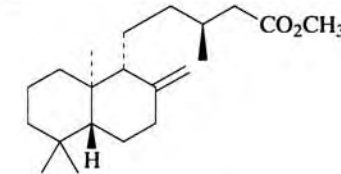
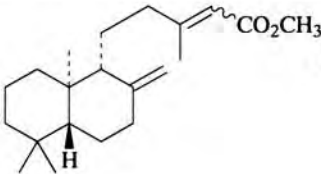
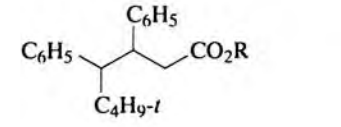
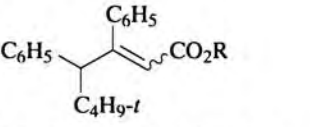
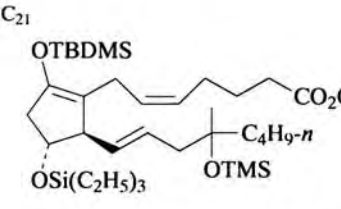
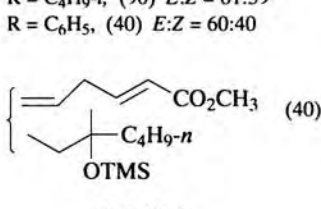
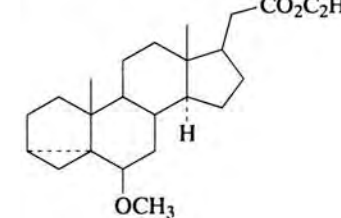
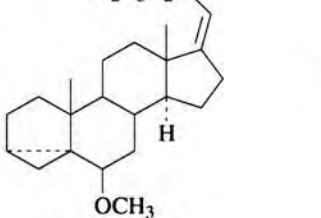
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LCA, THF, -78°, 30 min; Ph ₂ Se ₂ , HMPA, -78°, 1 h; 25° 2. H ₂ O ₂ (30%), Et ₂ O/THF (3:1), 0°, 1 h	 (72)	589
	A-1	1. LDA, THF; PhSeBr 2. H ₂ O ₂ , THF		590
	A-1	1. LCA, THF, -60°; Ph ₂ Se ₂ , THF, (90) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, rt, 4 h	 (40)	591
	A-1	1. LDA; PhSeCl, THF, HMPA, -78° (60) 2. C H ₃ CO ₃ H, THF, -5° to reflux	 (70)	592

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

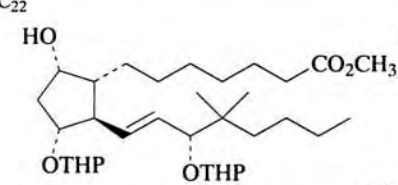
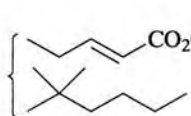
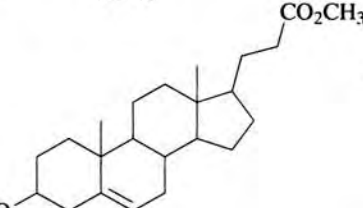
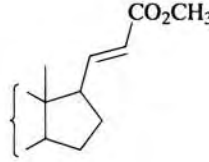
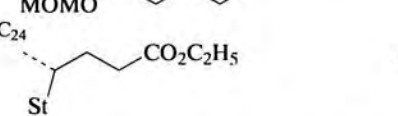
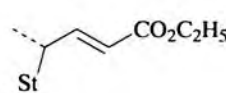
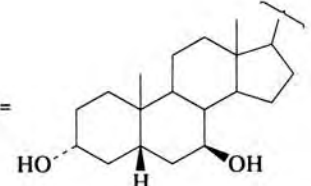
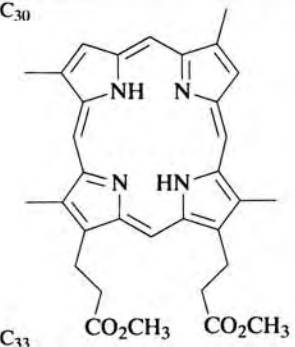
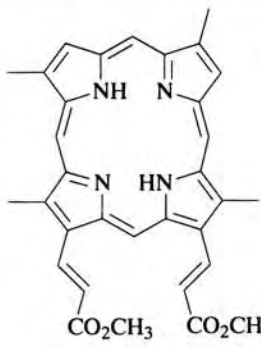
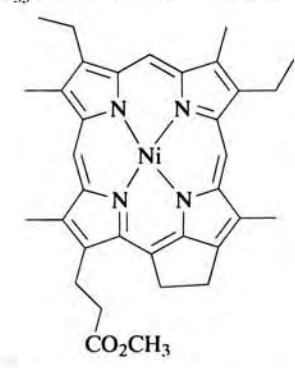
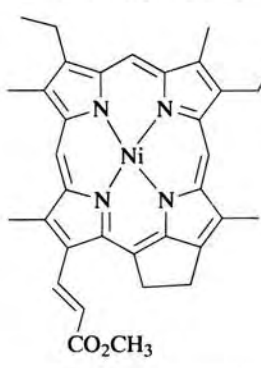
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
<p>C₂₂</p> 	A-1	1. LDA (2.2 eq), THF, -78°, 15 min; Ph ₂ Se ₂ , (1.5 eq) 2. H ₂ O ₂ (30%), THF, AcOH, 35°, 5 min	 (—)	593
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, 0° to rt	 (59)	594
<p>C₂₄</p> 	A-1	1. LDA, Ph ₂ Se ₂ , THF, -78°, 2 h (84) 2. H ₂ O ₂ , CH ₂ Cl ₂ , rt, 15 min	 (99)	354
<p>St =</p> 				

Table V. α,β -Unsaturated Carboxylic Esters (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
<p>C₃₀</p> 	A-1	1. LDA (4 eq), THF, -78°, 15 min; PhSeBr 2. H ₂ O ₂ (30%), AcOH, -78° to rt, 30 min	 (29)	595, 596
<p>C₃₃</p> 	A-1	1. [RSe] 2. [Ox]	 (—)	597

^a The yield was calculated by the present authors.

Table VIA. α,β -Unsaturated γ -Lactones

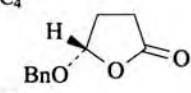
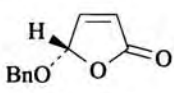
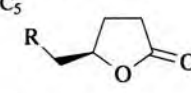
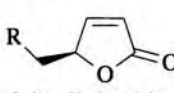
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	A-1	1. LDA, THF, Ph ₂ Se ₂ (59) 2. NaIO ₄ , MeOH, H ₂ O	 (85)	598
C ₅ 	A-1	1. LDA, THF, -78°, 35 min; PhSeBr, -78°, 1.5 h (62) 2. H ₂ O ₂ (30%), THF, AcOH	 I, R = H (quant)	599
	A-1	1. LDA, THF, -78°; PhSeBr, -78°, 3 h (46) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 30 min	I, R = OH (83)	600
	A-1	1. LDA, PhSeBr 2. NaIO ₄ , 18-crown-6, EtOAc, H ₂ O, 50°	I, R = Ph ₃ CO (82) I, R = Bn (50)	204, 168a 168a
	A-1	1. LiN(TMS) ₂ , THF; PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0°	I, R = TBDMSO (50)	601
	A-1	1. LiN(TMS) ₂ , THF; -78°; PhSeBr 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	I, R = TBDPSO (97)	168

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

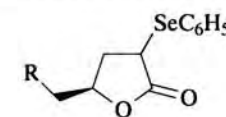

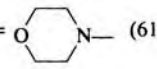
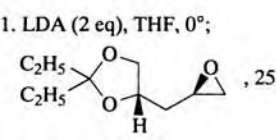
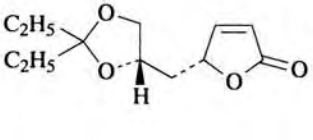
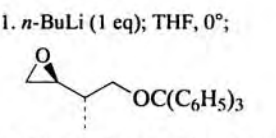
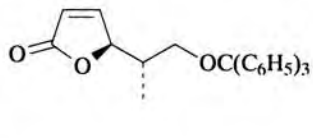
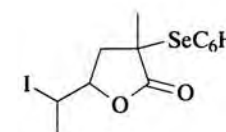
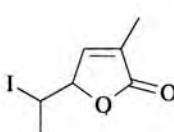
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	H ₂ O ₂ (30%), CH ₂ Cl ₂	I, R = TBDPSO (>72)	290
	D-1	H ₂ O ₂ (30%), THF, AcOH, 0°, 30 min	I, R = C ₂ H ₅ O (100)	182
			I, R = C ₆ H ₅ S (57)	182
			I, R = 1-Pyrrolyl (100)	182
C ₇ 			I, R =  (61)	182
C ₆ H ₅ Se-CH ₂ -CO ₂ H	D-1	1. LDA (2 eq), THF, 0°;  , 25° 2. EtN=C=N(CH ₂) ₃ NMe ₂ , DMAP 3. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°	 (71)	290, 602
	D-1	1. <i>n</i> -BuLi (1 eq); THF, 0°;  2. EtN=C=N(CH ₂) ₃ NMe ₂ , DMAP 3. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°	 (75)	603, 602
	D-1	H ₂ O ₂ , THF, AcOH, 0°	 (—)	604

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

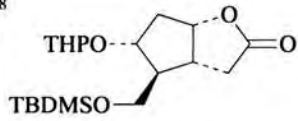
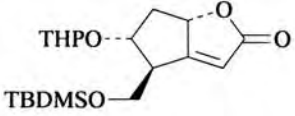
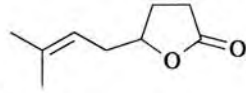
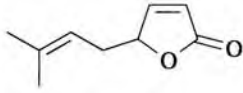
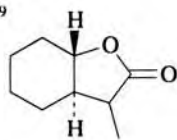
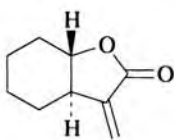
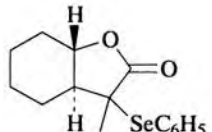
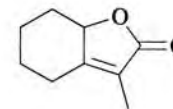
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, PhSeCl, THF, -78°, 30 min (86) 2. H ₂ O ₂ (10%), CH ₂ Cl ₂ , 37°, 1 h	 (79)	181
	A-1	1. LiN(TMS) ₂ , PhSeCl, THF, -70° 2. H ₂ O ₂ , CH ₂ Cl ₂ , rt	" (>33)	605
	A-1	1. LDA, THF, -78°; PhSeBr, -78° to rt 2. H ₂ O ₂ (30%, 6 eq), THF, AcOH	 (60)	606, 607
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA (85) 2. H ₂ O ₂ (30%), THF, AcOH	 I (96)	15
	D-1	H ₂ O ₂ (30%), THF, AcOH, 0°	I (80) +  (6)	53

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

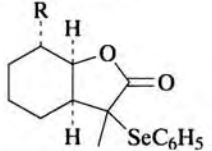
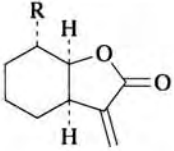
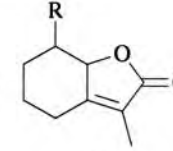
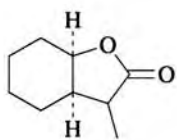
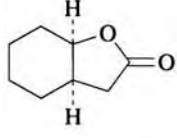
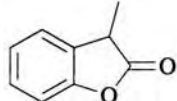
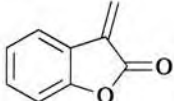
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	H ₂ O ₂ (30%), THF, AcOH, 0°	 I +  II	53
	D-1	H ₂ O ₂ (30%), THF, AcOH, 0°		I + II, R = I, (90) I:II = 100:0
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA (88) 2. H ₂ O ₂ (30%), THF, AcOH	I + II, R = H, (95) I:II = 1:9	15, 608
	D-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , THF, HMPA 2. LDA, THF, -78°, 1 h; MeI, HMPA 3. H ₂ O ₂ (30%), THF, AcOH, 0°	I + II, R = H, (high) I:II = 100:0	15
	A-1	1. LDA, PhSeBr 2. H ₂ O ₂	 (—)	177

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_{10} 	A-1	1. LCA, THF; PhSeBr, -78 to 25° 2. CH ₃ CO ₃ H (40%), EtOAc, 25°, 2 h	(56)	3
	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, HMPA, -78 to -40, 2 h R = Et (85), R = <i>n</i> -Bu (70) 2. H ₂ O ₂ (30%), AcOH, THF, 0°, 30 min	R = C ₂ H ₅ (96) R = <i>n</i> -C ₄ H ₉ (97)	608
	A-1	1. LDA, THF, -78°; PhSeBr, -78° to rt 2. H ₂ O ₂ (30%), THF	I R = H (10)	609
	D-1	H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	I, R = H (>73)	290
	D-1	H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py	I, R = CH ₃ (45)	610
C_{11} 	D-1	H ₂ O ₂ (30%), CH ₂ Cl ₂ , 30° to rt	(>69)	168
	A-1	1. LDA, THF, -78°, 30 min; Ph ₂ Se ₂ , HMPA, (1 eq), 0.5 h; -35°, 0.5 h (59), isomers 3:1 2. H ₂ O ₂ (30%), THF, AcOH, 0°	(37)	611

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 1.3 h; Ph ₂ Se ₂ , HMPA, (1 eq), 0.5 h; -35°, 0.5 h (32) 2. H ₂ O ₂ (30%), THF, AcOH, 0° to rt	(98)	611
	A-1	1. LDA, THF, -70°, 1.5 h; PhSeBr, -70° to rt 2. H ₂ O ₂ (35%, 5 eq), THF, AcOH, 5°	" (64)	612, 613
	A-1	1. LDA, -78°, Ph ₂ Se ₂ , 2 h 2. H ₂ O ₂ , THF, AcOH, 1.5 h	I, R = THP (30)	614
	A-1	1. LDA, THF, -78° to rt, 1.3 h; Ph ₂ Se ₂ , HMPA, -78 to -40°, 1.7 h (50) 2. HCl, H ₂ O, THF 3. H ₂ O ₂ (30%), THF, AcOH, 0°, 2 h	I, R = H (75)	161
	A-1	1. LDA, THF, -78°, 30 min; PhSeBr (25) 2. H ₂ O ₂ (30%), AcOH, H ₂ O, reflux	(60)	615

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LCA, THF, -78°, 15 min; PhSeBr, -78 to -10° 2. H ₂ O ₂ (30%), AcOH, 20°, overnight	 R = H (55) R = CH ₃ (—)	616
	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, HMPA, -78 to 40°, 2 h R = Et (70), R = <i>n</i> -Bu (80) 2. H ₂ O ₂ (30%), AcOH, THF, 0°, 30 min	 R = C ₂ H ₅ (80) R = <i>n</i> -C ₄ H ₉ (98) R = Bn (85)	608
	A-1	1. LDA, THF, -78°, 20 min; PhSeCl, HMPA, -78 to 40° R = <i>n</i> -Bu (72), R = Bn (83) 2. H ₂ O ₂ (30%), AcOH, THF, 0°, 30 min	 R = <i>n</i> -C ₄ H ₉ (99) R = Bn (85)	608
	A-1	1. LDA, THF, -70°; Ph ₂ Se ₂ , HMPA, -70 to -40° 2. H ₂ O ₂	 + 	320

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	H ₂ O ₂ , CH ₂ Cl ₂ , 0°, 30 min	 (>70)	617
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA 2. [Ox]	 (—)	58
	A-1	1. LDA, THF; PhSeCl 2. H ₂ O ₂ , <i>i</i> -Pr ₂ NEt	" (72)	617a
	A-1	1. LDA; THF, PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂	 (74)	43
	A-1	1. LDA, THF, -78°; PhSeCl (88) 2. H ₂ O ₂ (30%), SeO ₂ , AcOH, THF, 0°	 (70)	618

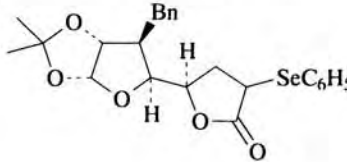
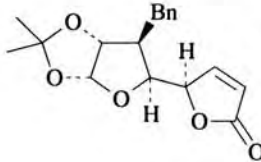
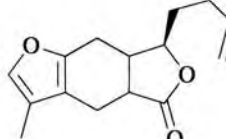
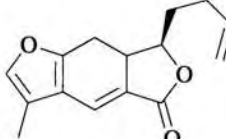
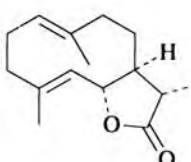
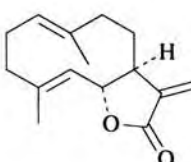
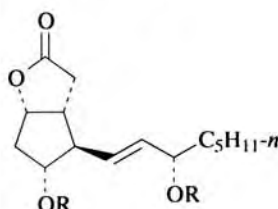
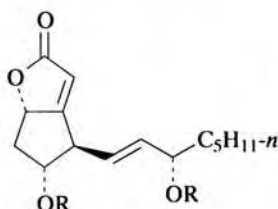
Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, -20° to rt 2. NaIO ₄ , NaHCO ₃	 (36) ^a	207
	A-1	1. LDA, Ph ₂ Se ₂ 2. H ₂ O ₂	 (70) ^b	619
	A-1	1. LDA, THF, -78°; PhSeBr, -78 to 0° 2. H ₂ O ₂ , H ₂ O, AcOH, 0° to rt	 (42)	580
	A-1	1. LDA, -78°; Ph ₂ Se ₂ 2. [Ox]	 (74)	620

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA (42) 2. H ₂ O ₂ (35%), THF, 0°	 (37) ^c	621
	D-1	1. LDA, THF, -78°; I ₂ ; DMSO, 140° (47) 2. CH ₃ CO ₃ H, THF, 0° to 25°	 (31)	622
	A-10	1. PhSeCl, MeCN, 25°, 40 min isomers 1:1 2. CH ₃ CO ₃ H (40%, 2 eq), CH ₂ Cl ₂ , 25°, 1 h (67)	 (92)	146
	A-1	1. LDA, THF, -78°, 1 h; PhSeBr, -78 to -40° 2. H ₂ O ₂ , AcOH (cat.), THF, 0°, 0.5 h	 (93)	623

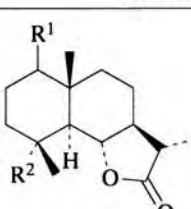
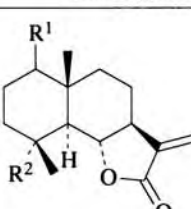
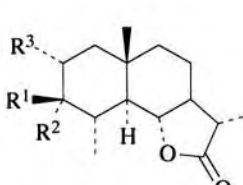
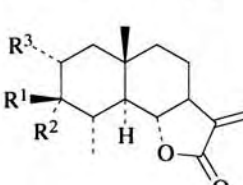
Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	H ₂ O ₂ (30%), CH ₂ Cl ₂	 (>75)	290
	A-1	1. LDA, THF, -78°, 40 min; PhSeCl, HMPA (60) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°, 1 h	 (38) ^b	624
	A-1	1. LDA, Ph ₂ Se ₂ 2. H ₂ O ₂	 (49)	625
	A-1	1. LDA, THF, -78°, 15 min; PhSeCl, 20 min (90) 2. H ₂ O ₂ (10%), CH ₂ Cl ₂ , rt, 1 h	 (—)	626

R = TBDMS

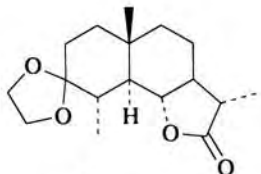
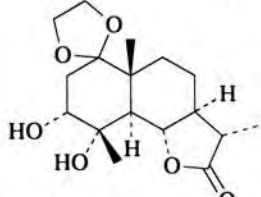
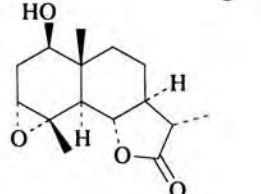
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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA (5 eq), THF, -78°, 1 h; Ph ₂ Se ₂ , HMPA, 15 min; -40°, 1 h (52) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 45 min	 I, R ¹ = R ² = OH (87)	117
	A-1	1. [PhSe] 2. [Ox]	I, R ¹ = OH, R ² = H (good)	118
	A-1	1. [PhSe] 2. [Ox]	I, R ¹ = H, R ² = OH (—)	118
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, -78 to -40° R ¹ = OH, R ² = H (60) R ¹ = H, R ² = OH (80) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	 I, R ¹ = OH, R ² = H, R ³ = Br (84) I, R ¹ = H, R ² = OH, R ³ = Br (91)	119 119

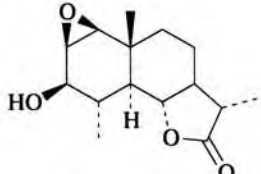
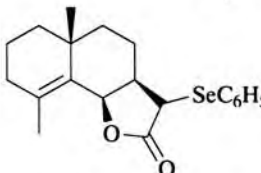
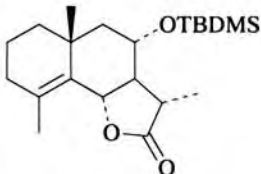
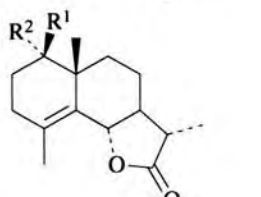
211

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA (2.4 eq), THF, -78°; Ph ₂ Se ₂ , HMPA, -78 to 40° 2. CrO ₃ , Py (16 eq), CH ₂ Cl ₂ , rt	I, R ¹ = H, R ² = O, R ³ = H (—)	216
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , THF, HMPA, -78 to -40° (96) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	I, R ¹ = R ² = O(CH ₂) ₂ O, R ³ = H (96)	160a
	A-1	1. LDA, THF; Ph ₂ Se ₂ , THF, HMPA, (96) 2. H ₂ O ₂ (50%), AcOH, reflux (97) 3. H ₂ O ₂ (30%), THF, AcOH, 0°	(93)	160a
	A-1	1. LDA (3.6 eq), THF, -78°, 100 min; Ph ₂ Se ₂ , HMPA, 40 min; -40°, 1 h (49) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 30 min	(84)	116
	A-1	1. LDA (3 eq), THF, -78°, 1 h; Ph ₂ Se ₂ , 15 min; -40°, 1.5 h (85) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 30 min	(86)	117

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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA; Ph ₂ Se ₂ (81) 2. MnO ₂ (60) 3. H ₂ O ₂ (30%), THF, AcOH	(75)	159
	D-1	1. LDA, THF, -78°; MeI, HMPA, -78 to -10° (94) 2. H ₂ O ₂ , THF, AcOH, 0°	(94)	627, 628
	A-1	1. LDA, THF, -78°; PhSeCl (82) 2. H ₂ O ₂ (30%), THF, AcOH, 0° to rt	(82)	629
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, -78 to -40° 2. H ₂ O ₂ (30%), THF, AcOH	R ¹ = OH, R ² = H (60) 113, R ¹ = H, R ² = OH (—) 160, 114	

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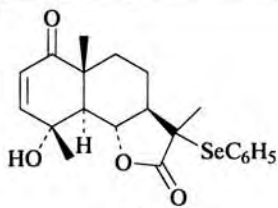
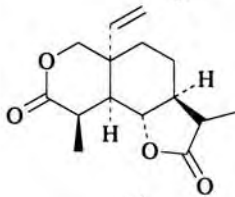
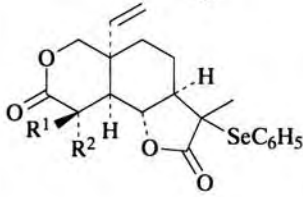
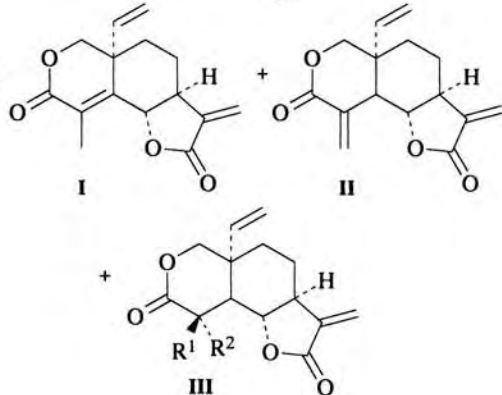
Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; Ph ₂ Se ₂ 2. H ₂ O ₂ , THF, AcOH	(50)	115
	A-1	1. LDA, THF; -78°; Ph ₂ Se ₂ , HMPA (21) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	(82)	630
	A-1	1. LDA (>2 eq), THF; -78°, 1 h; Ph ₂ Se ₂ , 40 min; -40°, 1 h (31) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 1 h	I, R = H (quant)	117

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

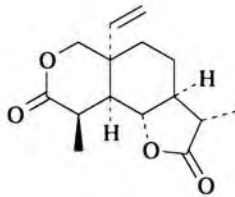
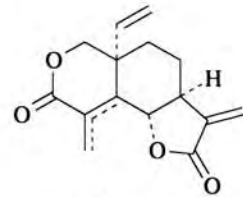
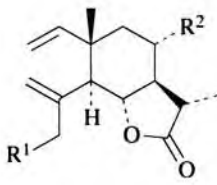
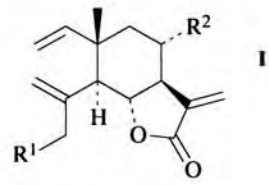
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; -78°, 1 h; Ph ₂ Se ₂ , HMPA 2. H ₂ O ₂ (30%), THF, AcOH, 0°	I, R = OH (—)	631
	A-1	1. LDA, THF; -78°; PhSeCl 2. O ₃ , CH ₂ Cl ₂ , -78°; 25°, 1 h	(60)	488
	A-1	1. LDA (2 eq); Ph ₂ Se ₂ (15) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	" (quant)	159
	A-1	1. LDA; Ph ₂ Se ₂ (66) 2. MnO ₂ (87) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	" (quant)	159

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	H ₂ O ₂ (30%), THF, AcOH, 0°	(—)	160
	A-1	1. LDA, HMPA, THF; Ph ₂ Se ₂ (90) 2. H ₂ O ₂ (30%), THF, 0° to rt	(84)	632, 633
	A-1	H ₂ O ₂ (30%), THF, 0° to rt		

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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
			R ¹ = CH ₃ , R ² = SC ₆ H ₅ , I:II:III = 10:30:60 (64)	632,
			R ¹ = SC ₆ H ₅ , R ² = CH ₃ , I:II:III = 0:86:0 (89)	633
	A-1	1. LDA (2 eq), THF, -78°; PhSeCl, HMPA, -40° (>90) 2. H ₂ O ₂ (30%), THF		634
			from β -selenide, 100% <i>exo</i> (82) from α -selenide, <i>exo:endo</i> = 25:62 (87)	
	A-1	1. LDA, THF; Ph ₂ Se ₂ , HMPA, -78 to -20° (97) 2. H ₂ O ₂ (30%, 2.2 eq), THF		634a
	A-1	1. LDA, THF, HMPA, -78°, 30 min; Ph ₂ Se ₂ , 30 min; 20°, 1 h (58) 2. H ₂ O ₂ (30%), THF, AcOH, 0°, 1 h	I , R ¹ = OH, R ² = H (92)	635

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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl, HMPA, -78 to -40° (61) 2. H ₂ O ₂ (30%), THF, rt	I, R ¹ = H, R ² = OTBDMS (84)	636
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, -78 to -40° (79) 2. H ₂ O ₂ (30%, 10 eq), THF, AcOH, 0°	(94)	20
	A-1	1. LDA, TMEDA, THF, -23°; PhSeCl, (66) 2. H ₂ O ₂ , THF, AcOH, 0°, 1 h	(74)	20
	A-1	H ₂ O ₂ or NaIO ₄	(81)	319
	A-1	O ₃ , CH ₂ Cl ₂ , -78°, 3 min; 0°, 1 h; Me ₂ S, rt, 2 h	(68)	319

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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, (17) 2. H ₂ O ₂ (35%), THF, 0°	(64)	637
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, (84) 2. H ₂ O ₂ (35%), THF, 0°	(quant)	637
	A-1	1. [PhSe] (42) 2. [Ox] ^o	exo (37) endo (31)	638, 20
	A-1	1. LDA, THF, -78°; PhSeCl, HMPA, (50) 2. H ₂ O ₂ (30%), THF, 0°	(85)	639
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), SeO ₂ , AcOH, THF, 0°	(51)	618

70:30

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Table VIA. α,β -Unsaturated γ -Lactones (Continued)

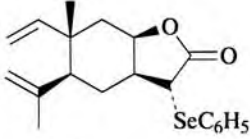
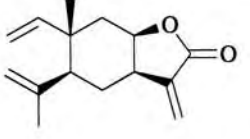
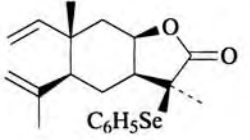
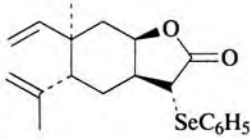
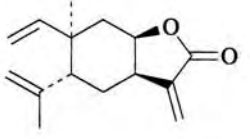
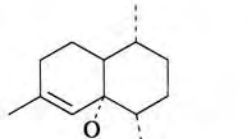
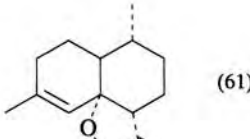
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. LDA, THF, -78°; MeI, HMPA, -78° to rt (84) 2. H ₂ O ₂ (30%), SeO ₂ , AcOH, THF, 0°	 (89)	618
	A-1	H ₂ O ₂	" (—)	639
	A-1	1. LDA, THF, -78°; MeI, HMPA, -78° to rt (74) 2. H ₂ O ₂ (30%), SeO ₂ , AcOH, THF, 0°	 (95)	618
	A-1	1. LDA, Ph ₂ Se ₂ , THF, HMPA, -78° (32) 2. H ₂ O ₂ (30%), AcOH, THF, 0°	 (61)	640

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

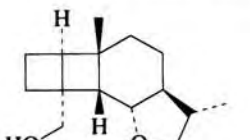
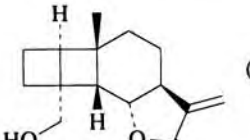
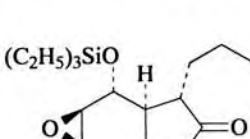
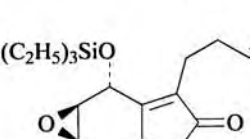
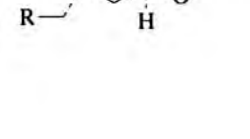
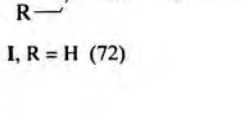

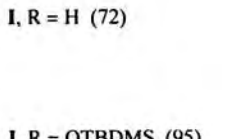
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeBr, THF, HMPA, -78 to 0° 2. H ₂ O ₂ (30%), AcOH, THF, 0°	 (64) ^b	580
	A-1	1. LTMP, THF, -10°, 1.5 h; 0°, 30 min; PhSeCl (2 eq), HMPA, -20° (49) 2. NaIO ₄ , THF, H ₂ O	 I, R = H (72)	58, 617a
	A-1	1. KN(TMS) ₂ , THF, -100°, 10 min; I, R = H (72) Ph ₂ Se ₂ , THF, HMPA; -20°; O ₂ , -78°, 1 h (72) 2. NaIO ₄ , THF, H ₂ O	 I, R = H (72)	58
	A-1	1. KN(TMS) ₂ , THF, -100°, 10 min; I, R = OTBDMS (95) Ph ₂ Se ₂ , HMPA, 1.5 h, -20°, 1 h; O ₂ , -78°, (82) 2. H ₂ O ₂ (15%), <i>i</i> -Pr ₂ NEt, 25°, 3 h; reflux 3 h	 I, R = OTBDMS (95)	58

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

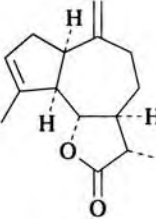
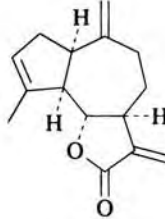
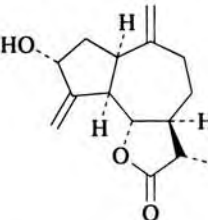
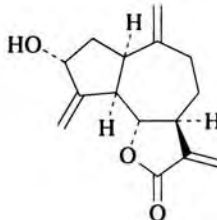
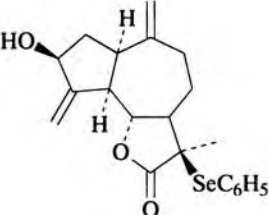
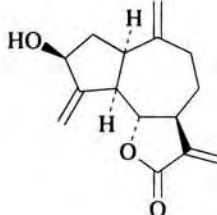
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 50 min; Ph ₂ Se ₂ , HMPA, 20 min; -35°, 1.5 h 2. H ₂ O ₂ (30%), AcOH, THF, 0°, 0.5 h	 (~64) ^d	641
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA, -70 to -30° (41) 2. H ₂ O ₂ (30%), AcOH, THF	 (89)	642
	—	H ₂ O ₂ (30%), AcOH, THF	 (84)	642

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

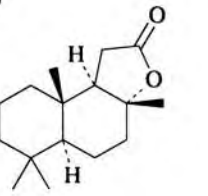
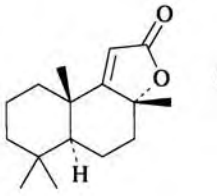
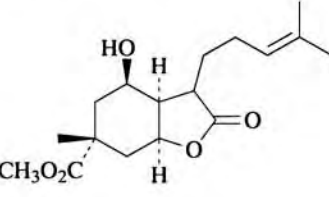
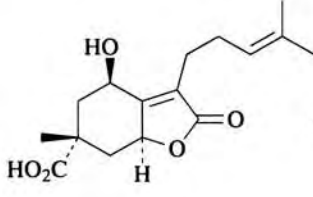
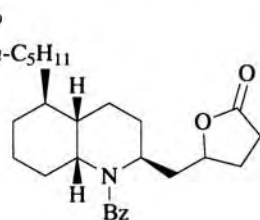
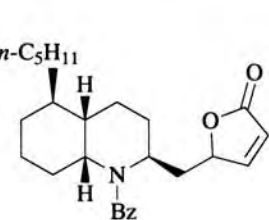
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LCA, THF, -60°, 1 h; PhSeBr, 1 h, rt 2. CH ₃ CO ₃ H (40%), EtOAc, rt, 2 h	 (—)	643
	A-1	1. LDA, HMPA, THF, -78 to -20°, 1.5 h; PhSeCl, -55 to -30° (65) 2. KOH/EtOH (10%) 2. H ₂ O ₂ (30%), AcOH, THF, 0° to rt	 (69)	163, 644
	A-1	1. LCA, THF, -73 to -40°; PhSeCl, -73° (87) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°	 (100)	645

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

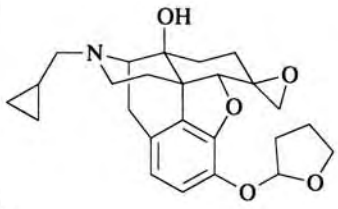
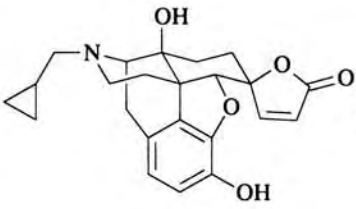
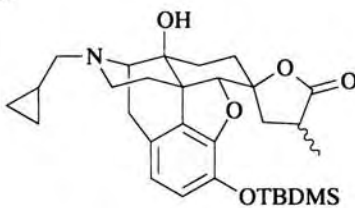
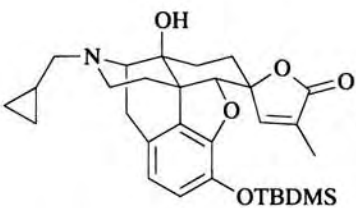
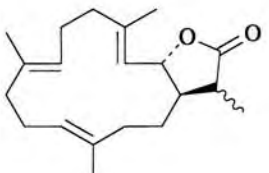
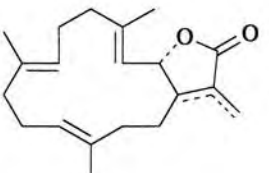
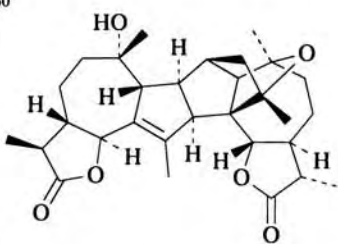
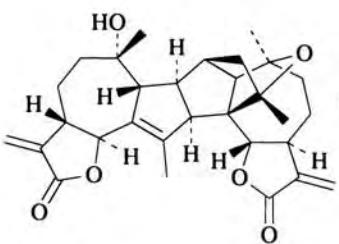
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. PhSeCH=C(OLi) ₂ ; HCl (17) 2. TBDMSCl, imidazole 3. NaIO ₄ 4. <i>n</i> -Bu ₄ NF	 (60)	646
	A-1	1. LDA, THF, -78 to -40°; PhSeCl (95) 2. NaIO ₄ , MeOH, H ₂ O, NaHCO ₃ , rt	 (84)	646
	A-1	1. LDA, PhSeCl, THF, -78° 2. NaIO ₄ , MeOH, rt	 <i>exo</i> (60) <i>endo</i> (12)	208

Table VIA. α,β -Unsaturated γ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. [PhSe] 2. [Ox]	 (—)	647

^a The paper reported an incorrect structure for the starting material.

^b The yield includes other steps.

^c The product was a 1:1 mixture of endo- and exocyclic olefins; the product shown (yomogin) was isolated in pure form.

^d The yield was calculated by the present authors.

Table VIB. α,β -Unsaturated δ -Lactones

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	A-1	1. LDA, THF, -75°; PhSeCl 2. [Ox]	(60)	648
C ₅ 	A-1	1. LDA, THF; PhSeCl 2. MCPBA, CH ₂ Cl ₂	(64)	649
C ₆ 	A-1	1. LDA, THF, -70°; PhSeCl 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°	A (18) B (37)	650
C ₇ 	A-1	1. LDA, THF, -70°; PhSeCl, -70° to rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	R = H (67) R = <i>i</i> -C ₃ H ₇ (70) R = <i>t</i> -C ₄ H ₉ (80)	650
C ₈ 	A-1	1. LDA, -78°; PhSeBr 2. H ₂ O ₂	(82)	651
R = CH ₂ O(CH ₂) ₂ OCH ₃				

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Table VIB. α,β -Unsaturated δ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₉ 	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%), THF, 0°	(73)	652
	D-1	1. LiN(TMS) ₂ , TsO-CHO 2. H ₂ O ₂ ; NaHCO ₃	(61)	653
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ , THF, 0°	(66)	654
C ₁₀ 	A-1	1. LDA, THF, -78°; PhSeBr (93% of two isomeric selenides A, B, 1.4:1) 2. MCPBA, CH ₂ Cl ₂ , CCl ₄ , -22° to rt	I + II from A: I (92) from B: I:II = 1:1.4 (quant)	655, 656

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Table VIB. α,β -Unsaturated δ -Lactones (Continued)

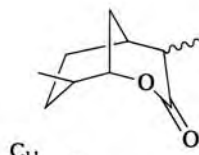
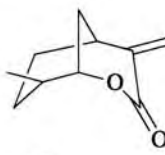
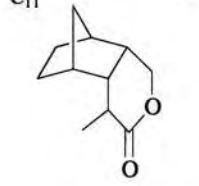
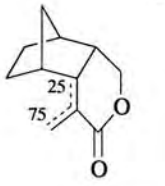
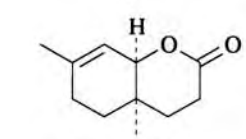
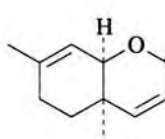
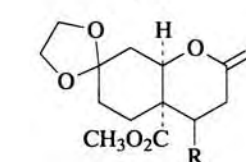
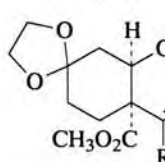
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, PhSeCl, HMPA 2. H ₂ O ₂	 (—)	657
	A-1	1. LDA, THF, -78°; Ph ₂ Se ₂ , HMPA (62) 2. H ₂ O ₂ (30%), THF, AcOH	 (99)	15
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ (30%), THF, AcOH, 0°	 (98)	658
	B-2	(PhSeO) ₂ , PhCl, 80 to 85°, 42 h	 (70)	88
R = β -CH ₃ R = α -CH ₃	A-1	1. LDA, PhSeCl, THF, -70°, 2 h; -5° 2. H ₂ O ₂ (30%), AcOH, rt, 1 h	" (49)	294

Table VIB. α,β -Unsaturated δ -Lactones (Continued)

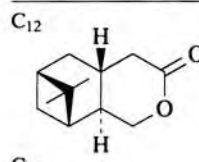
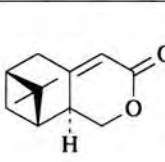
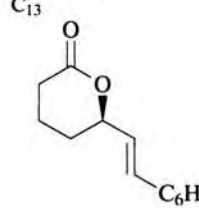
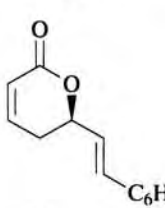
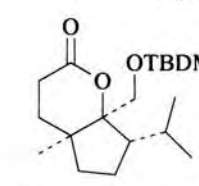
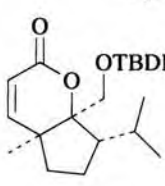
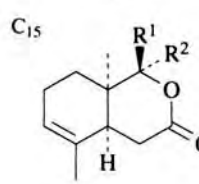
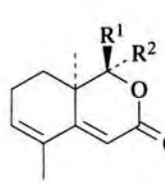
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeCl (80) 2. H ₂ O ₂ (30%), Et ₂ O, Py, reflux	 (—)	22
	A-1	1. LDA; PhSeBr 2. H ₂ O ₂	 (—)	659
	B-2	(PhSeO) ₂ O, PhCl, 135°	 (86) ^a	87
	A-1	1. LDA, THF, -78°; PhSeCl, THF, HMPA 2. H ₂ O ₂ (30%), THF, AcOH, 10 to 20°		660
			R ¹ = H, R ² = β -furyl (90) R ¹ = β -furyl, R ² = H (88)	

Table VIB. α,β -Unsaturated δ -Lactones (Continued)

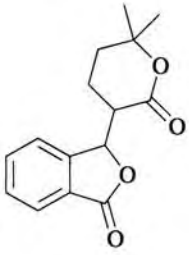
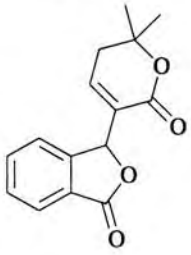
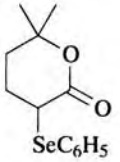
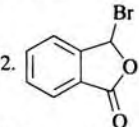
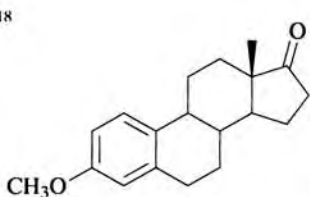
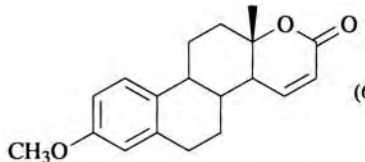
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, HMPA, THF, -78° to rt; Ph ₂ Se ₂ (15) 2. H ₂ O ₂ (30%), THF, AcOH, 0°	 (100)	293
	D-1	1. LDA  2. O ₃ , -78°; Et ₃ N; 25°	" (87)	292
	A-2	1. PhSeCl, EtOAc/CH ₂ Cl ₂ (1:5) (69) 2. H ₂ O ₂ , CH ₂ Cl ₂ /MeOH (1:32), 25°	 (66)	661, 199

Table VIB. α,β -Unsaturated δ -Lactones (Continued)

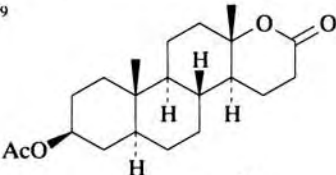
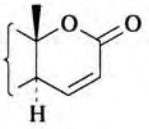
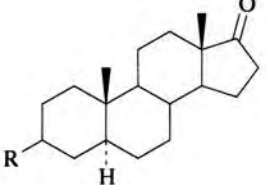
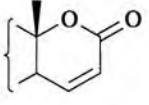
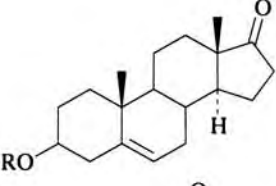
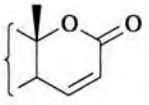
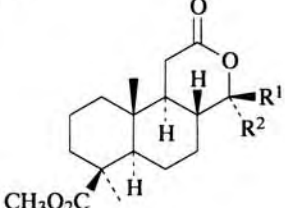
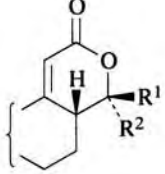
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	B-2	(PhSeO) ₂ O, PhSeCl, 100°, 2.5 h	 (80) ^b	86
	A-2	1. PhSeCl, EtOAc, 24 h 2. H ₂ O ₂ , EtOAc, THF	 R = OH (—) R = H (50)	199 200
	A-2	1. PhSeCl, EtOAc, rt, 18 h (64) 2. H ₂ O ₂ , CH ₂ Cl ₂ /MeOH (1:7)	 R = Ac (95) R = H (—)	200 199
	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ (30%)	 R ¹ = <i>i</i> -Pr, R ² = H (75) R ¹ = H, R ² = <i>i</i> -Pr (93)	242

Table VIB. α,β -Unsaturated δ -Lactones (Continued)

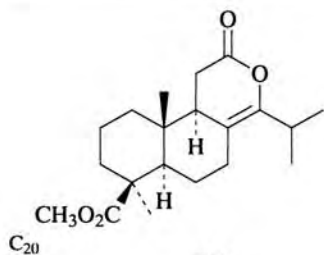
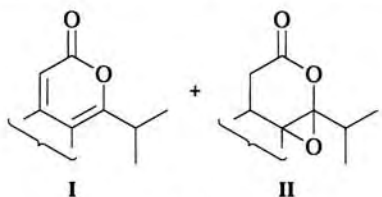
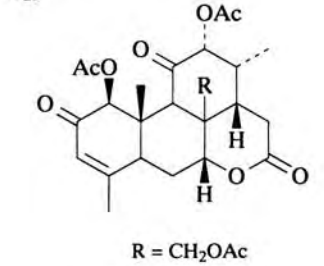
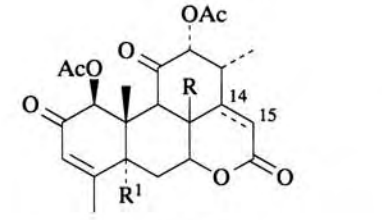
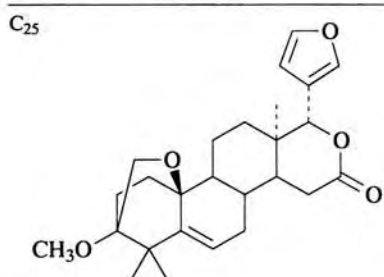
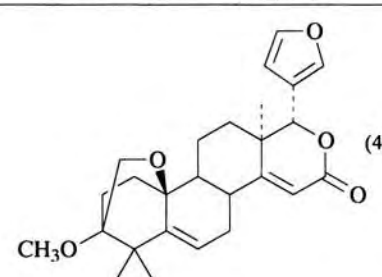
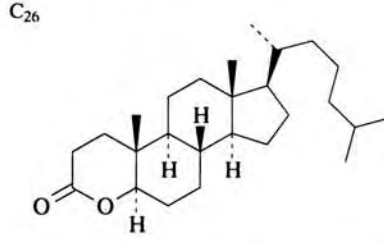
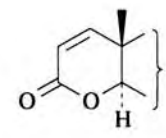
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₀</p>	A-1	1. LDA, THF, -78°; PhSeCl, 30 min 2. H ₂ O ₂ (30%)	 <p>(53) I:II = 82:9</p>	242
 <p>R = CH₂OAc</p>	B-2	(PhSeO) ₂ O, PhSeCl, 125°, 4 h	 <p>$\Delta^{14,15}$ R¹ = H (19) $\Delta^{14,15}$ R¹ = OH (16) R¹ = OH (20)</p>	233

Table VIB. α,β -Unsaturated δ -Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 <p>C₂₅</p>	A-1	1. LDA, HMPA, THF, -78°; PhSeCl, (52) 2. H ₂ O ₂ (30%), THF, 20°	 <p>(46)</p>	662
 <p>C₂₆</p>	B-2	(PhSeO) ₂ O, PhCl, 100°, 42 h	 <p>(90)</p>	86, 498

^a The yield includes other steps.

^b Two isomeric γ -hydroxylactones were formed, about 5% each.

Table VIC. α,β -Unsaturated ϵ -Lactones and Larger Rings

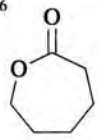
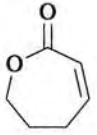
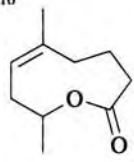
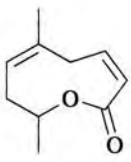
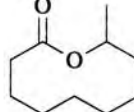
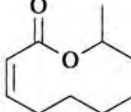
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°, 15 min PhSeBr 2. O ₃ , CH ₂ Cl ₂ , -78°; 25°	 (70)	2
	A-1	1. LDA, THF, HMPA, -70°; PhSeBr, -70 TO -60°, 15 min (50) 2. H ₂ O ₂ (30%), THF, 30°, 2.5 h	" (82)	663
	A-1	1. LDA, THF; PhSeBr 2. NaIO ₄ , MeOH	 (66)	209
	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ (30%), AcOH, 0°, 1 h	 (82)	40, 664

Table VIC. α,β -Unsaturated ϵ -Lactones and Larger Rings (Continued)

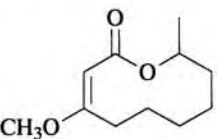
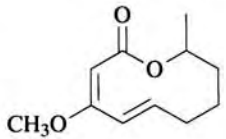
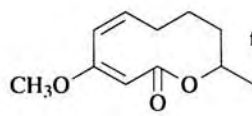
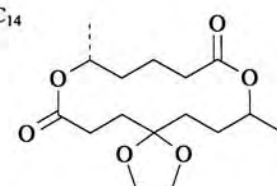
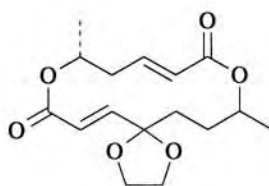
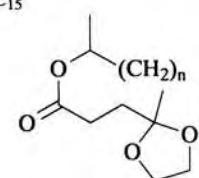
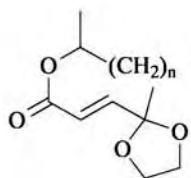
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	C-1	1. NBS, (PhCO ₂) ₂ , CCl ₄ , reflux 3 h; (32% isomer A, 58% B, unidentified) 2. Ph ₂ Se ₂ , NaBH ₄ , EtOH, 0°; 50°, 6 h; (67% selenide from A, 65% from B) 3. H ₂ O ₂ (30%), THF, rt, 3 h	 from A (95)	40
			 from B (100)	
	A-1	1. LDA, PhSeBr, THF, -78° 2. H ₂ O ₂ , aq. AcOH, 0°	 (50)	665
	A-1	1. LDA, THF, HMPA; PhSeBr 2. H ₂ O ₂ (15%), AcOH, 0°	 n = 9 (76) n = 10 (75)	666

Table VIC. α,β -Unsaturated ϵ -Lactones and Larger Rings (Continued)

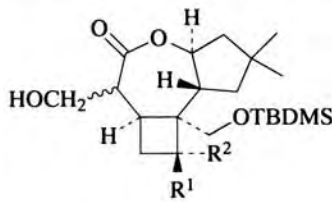
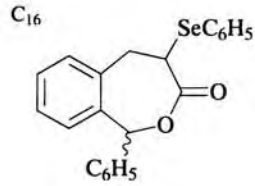
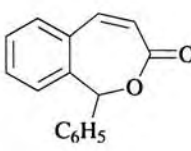
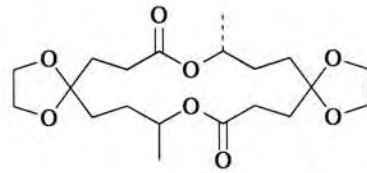
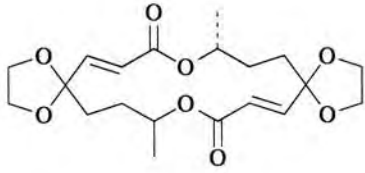
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA (2 eq); PhSeCl (48) 2. [Ox]	I , R ¹ = R ² = OC ₂ H ₅ (86)	667
	A-1	1. LDA, THF, -78°; PhSeCl (48) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 22°	I , R ¹ = OTHP, R ² = H (71)	667
	C-1	NaIO ₄ , MeOH, H ₂ O, THF, rt, 3.3 h	 (64)	668
	A-1	1. LDA, THF, PhSeBr, -78° 2. H ₂ O ₂ , AcOH, 0°, 2 h	 (46)	665

Table VIC. α,β -Unsaturated ϵ -Lactones and Larger Rings (Continued)

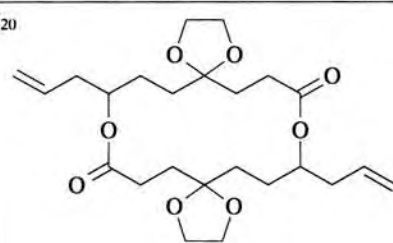
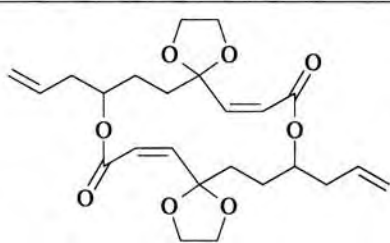
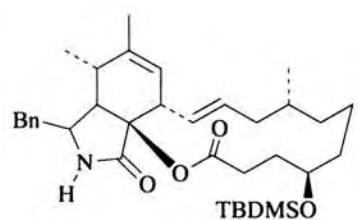
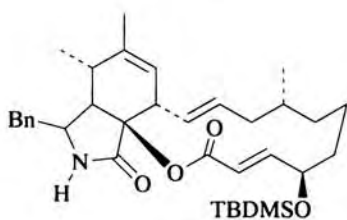
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; PhSeBr, -78° (14) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, 0°	 (86)	308
	A-1	1. LDA (3 eq), THF, -78°; PhSeCl (3 eq) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	 (70-76)	110

Table VII. α,β -Unsaturated Amides and Imides

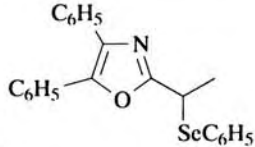
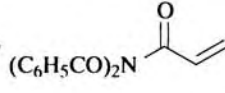
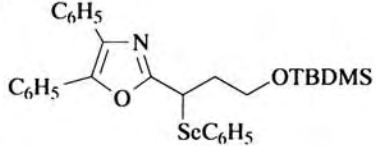
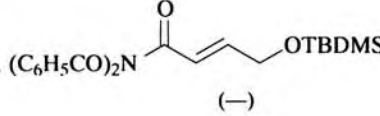
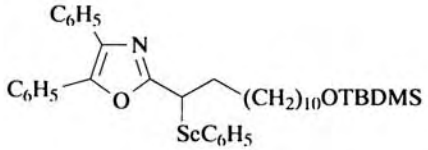
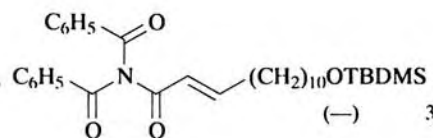
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₃ 	—	<i>meso</i> -Tetraphenylporphine, O ₂ , <i>hν</i> , CHCl ₃	 (nearly quant)	34
C ₄ 	—	<i>meso</i> -Tetraphenylporphine, O ₂ , <i>hν</i> , CHCl ₃	 (—)	34
C ₁₃ 	—	<i>meso</i> -Tetraphenylporphine, O ₂ , <i>hν</i> , CHCl ₃	 (—)	34

Table VIII. α,β -Unsaturated β -Lactams

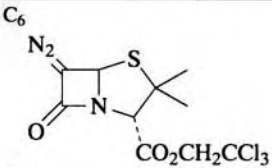
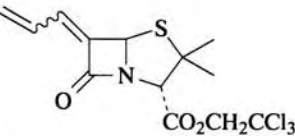
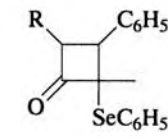
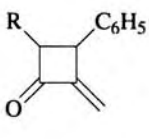
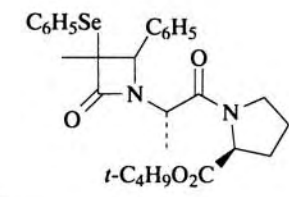
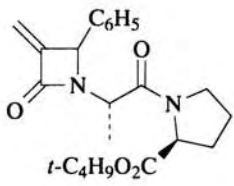
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 C ₆	—	1. PhSeCH ₂ CH=CH ₂ , Cu(acac) ₂ , CH ₂ Cl ₂ 2. MCPBA	 (70)	669
 C ₁₀	F-2	H ₂ O ₂ (28%), CH ₂ Cl ₂ , Py, 25°	 R = C ₆ H ₅ (92) R = CH ₃ (67) R = <i>t</i> -C ₄ H ₉ (85)	54
	F-2	H ₂ O ₂ (28%), CH ₂ Cl ₂ , Py, heat 2.5 h	 (24)	55

Table VIII.B. α,β -Unsaturated γ -Lactams

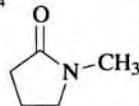
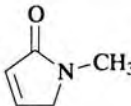
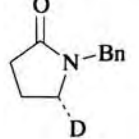
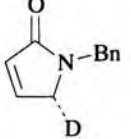
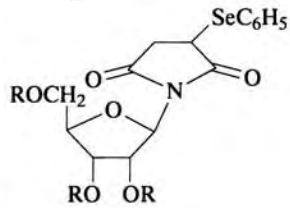
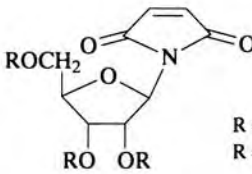
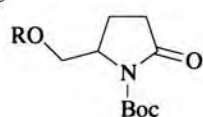
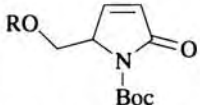
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA (2 eq), THF, HMPA, -78°; PhSeCl, -20 to 25° (55) 2. H ₂ O ₂ (30%), MeOH, 0°, 2 h	 (57)	309
	A-1	1. LDA, THF, HMPA, -78°, 10 min; PhSeCl, -78° to rt (56) 2. H ₂ O ₂ (30%), EtOAc, 0°, 30 min	 (84)	356
	—	MCPBA, CHCl ₃ , 0 to 25°, 1.5 h	 R = Ac (85) R = COC ₆ H ₅ (90)	670
	A-1	1. LDA, THF, PhSeCl, -78° 2. O ₃ , CH ₂ Cl ₂ , -78°; NaOAc, 0°	 I, R = TBDMS (70)	39
	A-1	1. LDA, THF, -78 to -20°; PhSeBr, -78° (79) 2. H ₂ O ₂ (30%), EtOAc, 15°	I, R = C(C ₆ H ₅) ₃ (80)	671

Table VIII.B. α,β -Unsaturated γ -Lactams (Continued)

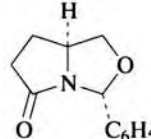
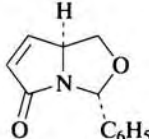
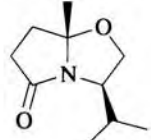
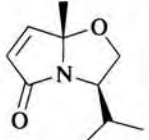
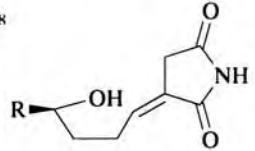
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF, -78°; PhSeBr (56) 2. O ₃ , CH ₂ Cl ₂ , -78°	 (quant)	672
	A-1	1. <i>s</i> -BuLi, THF, -78°; Ph ₂ Se ₂ , 2 h 2. H ₂ O ₂ , Py, 3 h	 (70)	673
	A-10	1. PhSeCl, MeCN, rt R = H (93), R = Me (80) 2. H ₂ O ₂ , THF, 0°; AcOH 2. O ₃ , CH ₂ Cl ₂ , -78°; Et ₃ N	I, R = H (99) I, R = H (95) I, R = CH ₃ (100)	145 145 674

Table VIII.B. α,β -Unsaturated γ -Lactams (Continued)

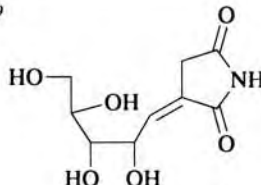
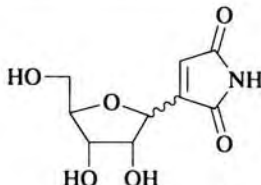
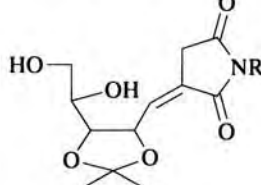
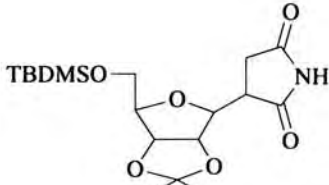
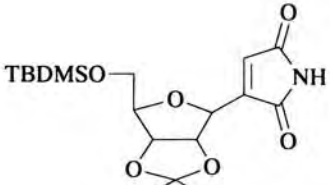
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_9 	A-10	1. PhSeCl, MeCN, reflux 2. H ₂ O ₂ , H ₂ O, MeCN	 (54) $\alpha:\beta = 41:13$	145, 674
	A-10	1. PhSeCl, MeCN, 0° 2. [Ox]	I , R = H, $\alpha:\beta = 3:1$ (—)	145
	A-10	1. PhSeCl (xs), K ₂ CO ₃ (xs) -78° to rt (17) 2. H ₂ O ₂ , THF, AcOH, 0°	I , R = C(C ₆ H ₅) ₃ , β only (76)	145
	A-1	1. LCA (3 eq), -78°, 20 min; PhSeCl (3.2 eq), -78° to -20° 2. NaIO ₄ , MeOH/H ₂ O (5:2); CCl ₄ , CaCO ₄ , reflux	 (90)	675

Table VIII.B. α,β -Unsaturated γ -Lactams (Continued)

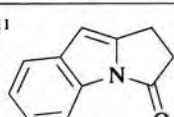
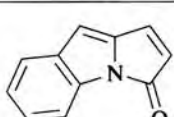
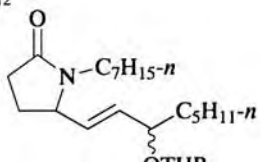
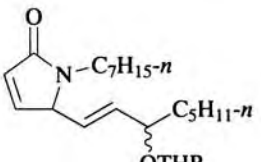
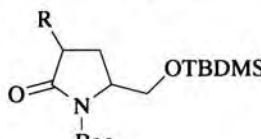
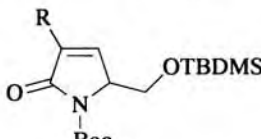
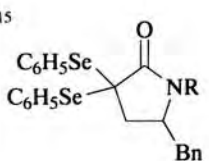
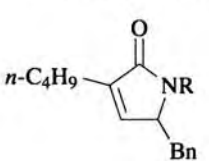
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_{11} 	A-1	1. LDA (2 eq), THF, -78°; PhSeCl, -78° to rt 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	 (39)	675a
C_{12} 	A-1	1. LDA (2 eq), THF, -78°; PhSeCl, -78 to 25° 2. MeOH, TsOH, 25°, 4 h 3. H ₂ O ₂ , MeOH, 0°, 1.5 h	 (74)	676
	A-1	1. LDA -78°; PhSeCl 2. H ₂ O ₂ (30%), 0°	 R = CH ₂ C ₆ H ₅ (—) R = CH ₂ CH=CHC ₆ H ₅ (—) R = CH ₂ CH=CHCH ₂ CH ₂ C ₆ H ₅ (—)	677
C_{15} 	D-1	1. <i>n</i> -BuLi, THF, 0°; <i>n</i> -BuI, 20° (67) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 0 to 20°	 I , R = H (70)	678

Table VIII.B. α,β -Unsaturated γ -Lactams (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	—	H ₂ O ₂ (2.5%), CH ₂ Cl ₂ , Py, 0 to 20°	I, R = COCH ₃ (64) I, R = COC ₆ H ₅ (75)	678
	D-1	1. LDA, THF, -78°; <i>n</i> -C ₄ H ₉ I, 20° (86) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py, 20°, 45 min	(84)	678
	A-1	1. LDA; PhSeCl (93) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	(100)	188
	—	1. PhSeCl, THF, 25°, 1 h (62) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 5°, 15 min	(73)	679

Table VIII.B. α,β -Unsaturated γ -Lactams (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	D-1	1. <i>n</i> -C ₄ H ₉ Li, Et ₂ O, 0°; <i>n</i> -C ₇ H ₁₅ Br, 20° (27) 2. H ₂ O ₂ (2.5%), CH ₂ Cl ₂ , Py, 0 to 20°	(77)	678
	A-1	1. <i>n</i> -C ₄ H ₉ Li; Ph ₂ Se ₂ 2. NaIO ₄	 R ¹ = R ² = CH ₃ (—) R ¹ , R ² = CH ₂ (—)	680

Table VIII.C. α,β -Unsaturated δ -Lactams

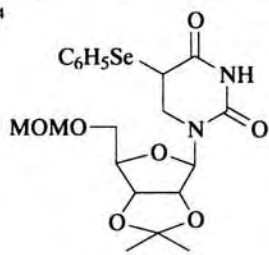
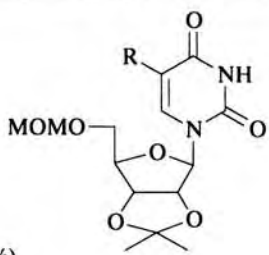
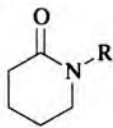
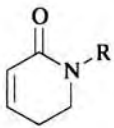
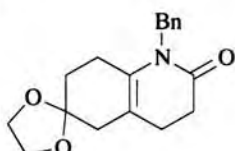
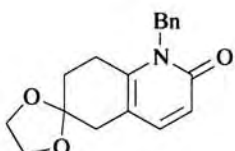
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.										
<p>C₄</p> 	D-1	1. LDA, THF, -70°, 1 h; RX, THF, -70°, 3-24 h 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	 (94) (96) (97) (91)	290a										
		<table border="1"> <thead> <tr> <th>RX</th> <th>Selenide Yield (%)</th> </tr> </thead> <tbody> <tr> <td>CH₃I</td> <td>(87)</td> </tr> <tr> <td>CH₂=CHCH₂Br</td> <td>(69)</td> </tr> <tr> <td>C₆H₅CH₂Br</td> <td>(72)</td> </tr> <tr> <td>CH₃O₂CCH₂Br</td> <td>(79)</td> </tr> </tbody> </table>	RX	Selenide Yield (%)	CH ₃ I	(87)	CH ₂ =CHCH ₂ Br	(69)	C ₆ H ₅ CH ₂ Br	(72)	CH ₃ O ₂ CCH ₂ Br	(79)		
RX	Selenide Yield (%)													
CH ₃ I	(87)													
CH ₂ =CHCH ₂ Br	(69)													
C ₆ H ₅ CH ₂ Br	(72)													
CH ₃ O ₂ CCH ₂ Br	(79)													
<p>C₅</p> 	A-1	1. LDA, PhSeCl R = Bn (53), R = <i>p</i> -MeOC ₆ H ₄ CH ₂ (94) 2. MCPBA	 R = C ₆ H ₅ CH ₂ (61) R = <i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ (78)	681										
<p>C₉</p> 	A-1	1. LDA, PhSeCl, THF, -78° 2. NaIO ₄ ; Et ₃ N, MeOH, reflux	 (80)	682										

Table VIII.C. α,β -Unsaturated δ -Lactams (Continued)

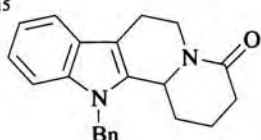
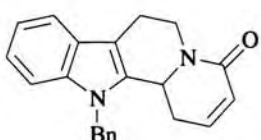
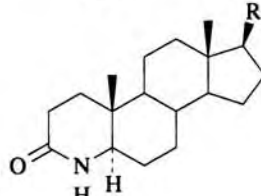
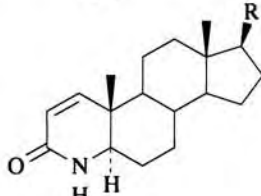
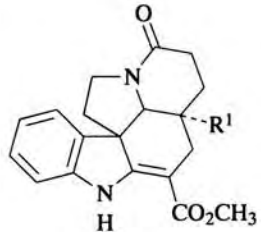
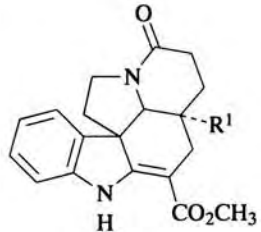
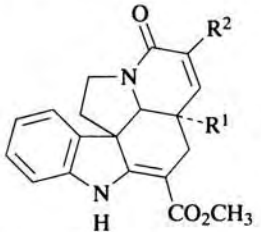
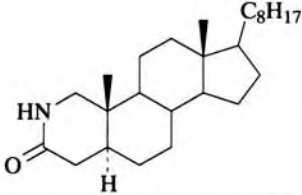
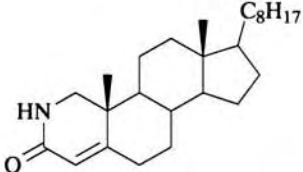
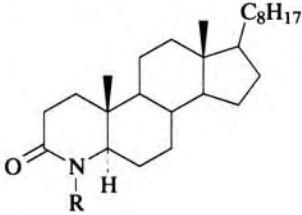
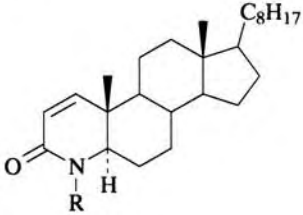
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
<p>C₁₅</p> 	A-1	1. LDA (3 eq), THF, -78°; PhSeCl 2. NaIO ₄ (4 eq), H ₂ O, MeOH, 25°	 (65)	206
				
<p>C₁₈ C₂₀</p> 	B-2	(PhSeO) ₂ O, diglyme, 120°, 23 h	R = OAc (64)	91
	B-2	(PhSeO) ₂ O, diglyme, 120°, 16 h	R = CH(OAc)CH ₃ (56)	91
	A-1	1. LDA (2 eq), THF, HMPA; PhSeCl (xs) (47) ^a 2. MCPBA	 I, R ¹ = C ₂ H ₅ , R ² = SeC ₆ H ₅ (88)	683

Table VIII.C. α,β -Unsaturated δ -Lactams (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
		After step 1: PhSH, base (85) ^b	I, R ¹ = C ₂ H ₅ , R ² = H (38)	683
	A-1	1. LDA (2 eq), THF, HMPA, -78°, 40 min; PhSeCl, -78°, 30 min (63) 2. MCPBA, CH ₂ Cl ₂ , -78°, 10 min	I, R ¹ = CH=CH ₂ , R ² = H (93)	287
C ₂₆ 	B-2	(PhSeO) ₂ O (2.3 eq), diglyme, 120°, 21 h	 (53)	91
	B-2	(PhSeO) ₂ O, diglyme, 120°, 14 h	I, R = H (88)	91
	B-2	(PhSeO) ₂ O, diglyme, 120°, 3 h	I, R = COC ₆ H ₅ (35) + 29% of R = H	91
			 I	

^a The yield is of the α,α -bis(phenylseleno)lactam.

^b This step converts the α,α -bis(phenylseleno)lactam to the α -phenylselenolactam.

Table VIIIID. α,β -Unsaturated ϵ -Lactams and Larger Rings

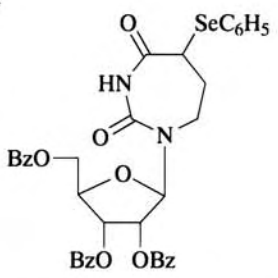
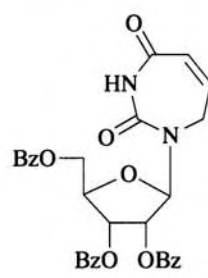
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	—	MCPBA, CHCl ₃ , rt, 15 min; Et ₂ NH, reflux 15 min	 (63)	684

Table IX. Dehydroamino Acids and Derivatives

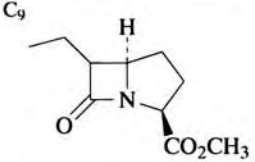
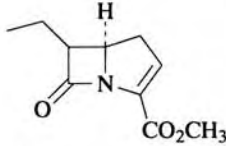
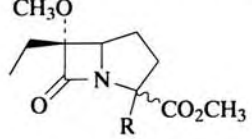
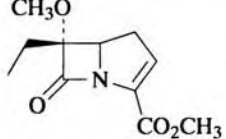
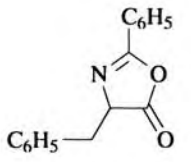
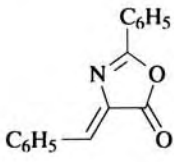
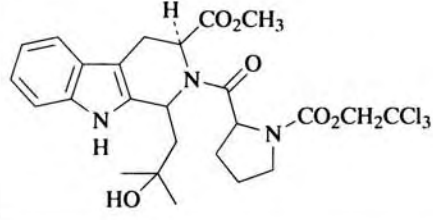
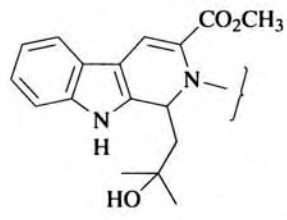
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LiN(TMS) ₂ , THF, -78°; PhSeBr 2. MCPBA, CH ₂ Cl ₂ ; Et ₃ N	 (32)	685
	A-1	1. LDA; PhSeCl (61) 2. MCPBA; Et ₃ N	 I, R = H (good)	362
	A-8	1. Ph ₂ Se ₂ , NaI (2 eq), HMPA, 80°, 2 h (50) 2. MCPBA; Et ₃ N	I, R = CO ₂ CH ₃ (good)	362
	A-2	1. PhSeCl, EtOAc, rt, 8 h; reflux 6 h; Et ₃ N 2. H ₂ O ₂ (30%), EtOAc, rt, 4 h	 (21)	344
	B-1	1. KH, THF, -3° 2. (PhSeO) ₂ O, THF, DMSO	 (35)	230

Table X. α,β -Unsaturated Nitriles

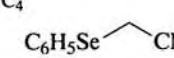
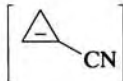
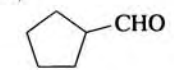
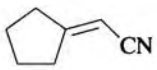
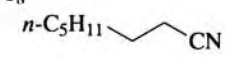
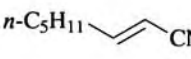
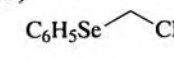
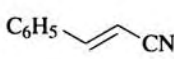
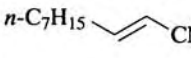
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	D-1	1. BrCH ₂ CH ₂ Br, <i>n</i> -Bu ₄ NI, NaOH, H ₂ O, 25°, 8 h (80) 2. NaIO ₄ , H ₂ O, MeOH, (60) 3. Anthracene, xylene, reflux 6 h	 (45) ^a	57
C ₇ 	G-2	1. <i>o</i> -O ₂ NC ₆ H ₄ SeCN, <i>n</i> -Bu ₃ P (89) 2. H ₂ O ₂ , THF	 (95)	37
C ₈ 	A-1	1. LCA (2 eq), THF, -75 to 25°; Ph ₂ Se ₂ , 25°, 1.5 h 2. H ₂ O ₂ (30%), THF, EtOAc, rt, 2 h	 (96) <i>E:Z</i> = 54:46	38
C ₉ 	D-1	1. PhCH ₂ X, <i>n</i> -Bu ₄ NI, NaOH, H ₂ O (96) 2. NCS (2.2 eq), MeCN-H ₂ O (60%), rt, 3 h or 2. H ₂ O ₂ (35%, 10 eq), THF	 (85) <i>E:Z</i> = 78:22 " (97) <i>E:Z</i> = 80:20	57 57
C ₁₀	D-1	1. <i>n</i> -C ₈ H ₁₇ X, <i>n</i> -Bu ₄ NI, NaOH, H ₂ O (92) 2. NCS (2.2 eq), MeCN-H ₂ O (60%), 25°, 3 h or 2. H ₂ O ₂ (35%, 10 eq), THF	 (93) <i>E:Z</i> = 55:45 " (91) <i>E:Z</i> = 61:39	57 57

Table X. α,β -Unsaturated Nitriles (Continued)

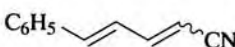
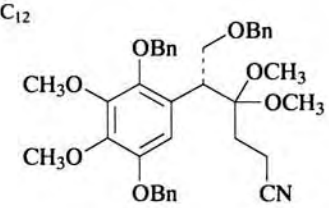
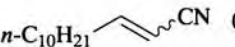
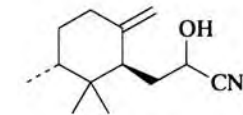
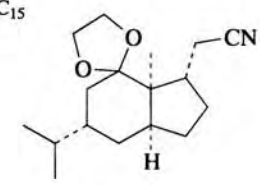
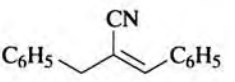
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₁	D-1	1. PhCH=CHCH ₂ X, <i>n</i> -Bu ₄ NI, NaOH, H ₂ O, 25°, 3-10 h (81) 2. NCS (2.2 eq), MeCN-H ₂ O (60%), 25°, 3 h or 2. H ₂ O ₂ (35%, 10 eq), THF	 (91) <i>E:Z</i> = 42:58	57
C ₁₂	A-1	1. LDA, THF, -78°; PhSeBr 2. H ₂ O ₂ , THF, EtOAc, rt	 (77) <i>E</i> only	686
C ₁₃	G-2	1. <i>o</i> -O ₂ NC ₆ H ₄ SeCN, <i>n</i> -Bu ₃ P 2. H ₂ O ₂ , THF	 (93) <i>E:Z</i> = 55:45	37
	C-1	1. MeSO ₂ Cl, Py; PhSeNa, EtOH (86) 2. H ₂ O ₂ , CH ₂ Cl ₂ , Py	 (88) <i>E:Z</i> = 82:18	124

Table X. α,β -Unsaturated Nitriles (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₅	A-1	1. LCA (2 eq), THF, -78°, 45 min; Ph ₂ Se ₂ , 25°, 2 h 2. H ₂ O ₂ (30%), EtOAc/THF (2:1), 25°, 2 h	 (42)	687
C ₁₆	D-1	1. PhCH ₂ X, <i>n</i> -Bu ₄ NI, NaOH, H ₂ O, 25°, 7-20 h (88) 2. NCS (2.2 eq), MeCN-H ₂ O (60%), 25°, 3 h	 (77)	57

^a The product was isolated as the Diels-Alder adduct with anthracene.

Table XIA. α,β -Unsaturated β -Keto Aldehydes

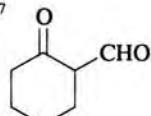
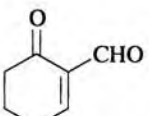
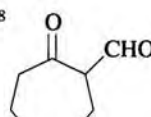
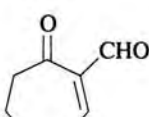
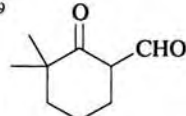
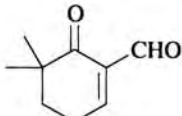
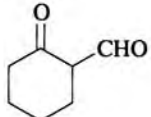
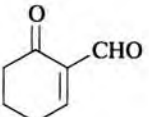
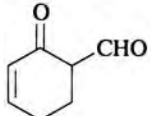
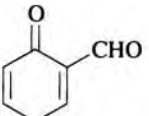
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₇ 	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	 (85)	97
C ₈ 	A-1	1. PhSeNEt ₂ , CHCl ₃ , 1 min (90) 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂ , 20-30°, 20 min	 (74)	64,41
C ₉ 	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0° 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	 (84)	97
	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0° 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	 (85)	97
	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0° 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	 (95)	97

Table XIA. α,β -Unsaturated β -Keto Aldehydes (Continued)

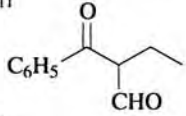
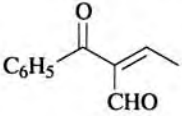
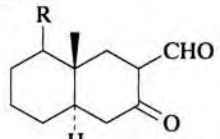
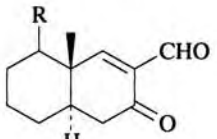
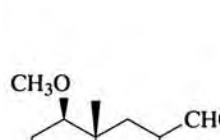
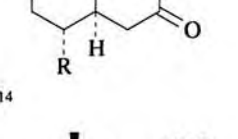
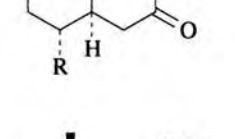
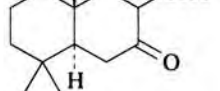
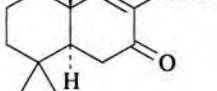
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₁ 	A-1	1. PhSeNEt ₂ , CHCl ₃ , rt, 1 min (89) 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂ , 20-30°, 20 min	 (35)	41
C ₁₂ 	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0 to 20°, 1 h 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0 to 20°, 45 min	 I, R = H (—)	359
	A-1	1. PhSeCl, Py, CHCl ₃ , 0°, 30 min 2. H ₂ O ₂ (30%), CHCl ₃	I, R = OTBDMS (72)	688
	A-1	1. PhSeCl, Py, CHCl ₃ , 0° 2. H ₂ O ₂ (30%)	 R = H (80) R = CH ₃ (77)	689
C ₁₄ 	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0 to 20°, 1 h 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0 to 20°, 45 min	 (96)	359

Table XIA. α,β' -Unsaturated β -Keto Aldehydes (Continued)

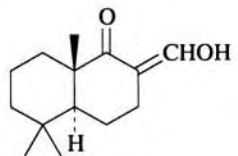
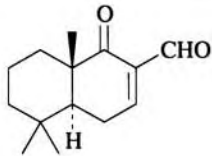
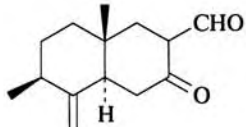
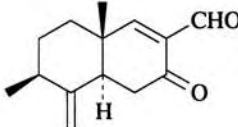
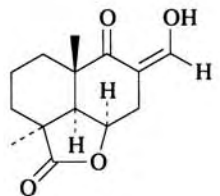
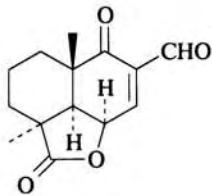
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. PhSeCl, Py, CHCl ₃ , 0° 2. H ₂ O ₂ (30%), 0°	 (100)	97, 690
	A-1	1. PhSeCl, Py, CH ₂ Cl ₂ , 0 to 20°, 1 h 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0°, 45 min	 (93)	359
	A-1	1. PhSeCl, Et ₃ N, THF, 10 min 2. MCPBA (85%), THF, 5 min	 (>54)	691

Table XIB. α,β' -Unsaturated β -Diketones

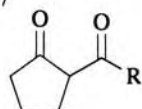
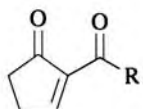
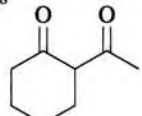
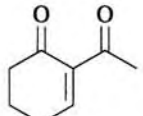
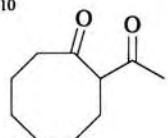
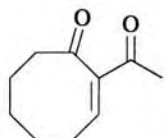
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₇ 	A-6	1. NaH, HMPA (3 eq), THF, 0°; Se ⁰ , rt, 12-24 h; MeI, 0°, 2 min R = Me (72), R = Et (84) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0 to 25°	 R = CH ₃ (69) R = C ₂ H ₅ (96)	62
C ₈ 	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. O ₃ , CH ₂ Cl ₂ , -78°; Py, CH ₂ Cl ₂ , rt	 (84)	2, 217
	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂	" (84)	2
	A-2	1. PhSeNMe ₂ , CHCl ₃ , rt (92) 2. MCPBA (2 eq) CH ₂ Cl ₂ , rt	" (85)	2,41
	A-6	1. NaH, HMPA (3 eq), THF, 0°; Se ⁰ , rt, 12-14 h; MeI, 0°, 2 min 2. MCPBA	" (83)	62
C ₁₀ 	A-1	1. [PhSe] 2. [Ox]	 (—)	692

Table XIB. α,β' -Unsaturated β -Diketones (Continued)

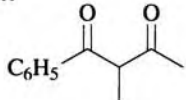
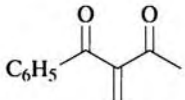
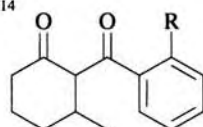
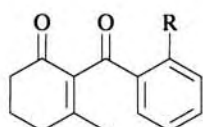
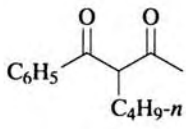
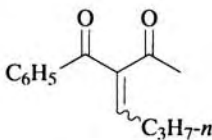
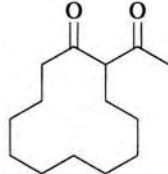
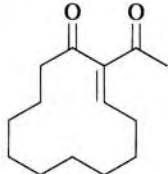
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_{11} 	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° (93) 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂	 (80)	2
C_{14} 	A-1	1. NaH, THF, rt, 2 h; PhSeCl, overnight R = H (58), R = OMe (60) 2. MCPBA (2 eq), CH ₂ Cl ₂	 R = H (73) R = OCH ₃ (58)	313
	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° (96) 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂	 (93)	2
	A-1	1. [PhSe] 2. [Ox]	 (—)	692

Table XIC. α,β' -Unsaturated β -Keto Esters, Acids, and Lactones

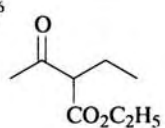
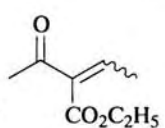
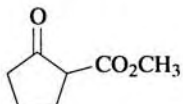
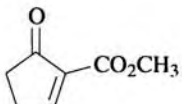
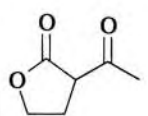
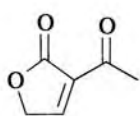
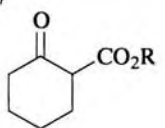
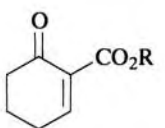
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₆ 	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. H ₂ O ₂ (15%, 2.5 eq), 30°, 20 min	 (86) <i>E:Z</i> = 4:1	693
	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂	 (81)	2
	A-1	1. NaH, THF; PhSeCl 2. O ₃ , CH ₂ Cl ₂ , -78°; rt	" (—)	694, 695
	A-2	1. PhSeCl, Py, CH ₂ Cl ₂ (100) 2. H ₂ O ₂ (28%), 0°	" (96)	358
	A-6	1. NaH, HMPA (3 eq), THF, 0°, Se ⁰ , 25°, 12-24 h; MeI, 0°, 2 min (82) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0 to 25°, 15 min	 (82)	62
C ₇ 	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂	 I I , R = CH ₃ (89)	2

Table XIC. α,β -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

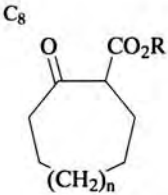
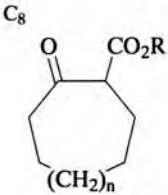
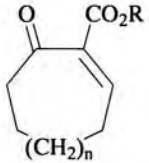
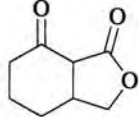
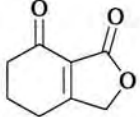
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.		
	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° (93) 2. H ₂ O ₂ (15%, 2.5 eq), CH ₂ Cl ₂ , <30°	I, R = C ₂ H ₅ (90)	693		
	A-2	1. PhSeCl, Py, CH ₂ Cl ₂ , 0°, 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	I, R = CH ₃ (98)	97		
	A-1	1. NaH, THF, 0°, 15 min; PhSeCl, 0° 2. H ₂ O ₂ (15%, 2 eq), CH ₂ Cl ₂ , Py	 I			
	<u>Selenide Yield (%)</u>					
	(90)				I, n = 1, R = CH ₃ (93)	2,217
	(96)				I, n = 2, R = CH ₃ (93)	2,217
	(96)				I, n = 3, R = C ₂ H ₅ (85)	693
(91)		I, n = 6, R = C ₂ H ₅ (91) <i>E:Z</i> = 1:1	693			
(90)		I, n = 9, R = C ₂ H ₅ (95)	693			
	A-2	1. PhSeCl, Py, CH ₂ Cl ₂ , 0°, 15 min 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 40 min	 (85)	97		

Table XIC. α,β -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

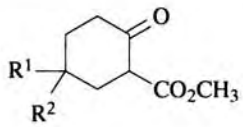
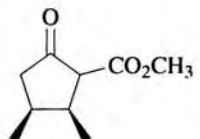
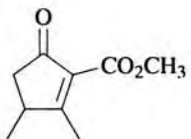
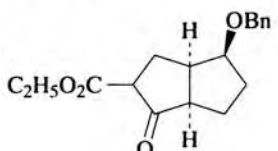
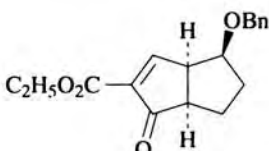
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. NaH, THF, -78°; PhSeCl (96-100) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0° to rt	I, R ¹ = CH ₃ , R ² = H (83-90)	696
	A-2	1. PhSeCl, Py, CH ₂ Cl ₂ , 0° 2. H ₂ O ₂ (30%), 0°	I, R ¹ = CH ₃ , R ² = CH ₃ (96)	697
	A-1	1. PhSeCl, NaH, THF, 0° to rt (93) 2. H ₂ O ₂ , CH ₂ Cl ₂ , 0° to rt	I, R ¹ = <i>i</i> -C ₃ H ₇ , R ² = H (98)	357
	A-1	1. NaH, PhSeCl, THF, 0°, 10 min 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , rt, 30 min	 (73)	698
	A-1	1. NaH, PhSeCl 2. H ₂ O ₂	 (60)	699

Table XIC. α,β' -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₀ 	A-1	1. NaH, THF, 0°; PhSeBr, 0 to 25° (88) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , 20 to 30°	(93)	700, 701
C ₁₁ 	A-2	1. PhSeNMe ₂ , CHCl ₃ , rt (92) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , 20 to 30°, 20 min	(98)	41
C ₁₂ 	A-1	1. KH, THF, 0°; PhSeCl 2. H ₂ O ₂ (30%), CH ₂ Cl ₂	(73)	702
C ₁₃ 	A-1	1. NaH, THF, 0°, 15 min; PhSeCl (79) 2. H ₂ O ₂ (10%, 2 eq), 20 to 30°, 20 min	(96)	703
C ₁₄ 	A-1	1. LDA (2.5 eq), THF, -78°; PhSeBr (76) ^a 2. O ₃ , CH ₂ Cl ₂ , -78 °	(77)	25

Table XIC. α,β' -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. [PhSe] 2. [Ox]	(—)	692
C ₁₅ 	A-1	1. LDA, THF, -78°; PhSeCl, 10 min (>37) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , 25°, 30 min	I, R ¹ = R ² = OC ₂ H ₅ (96)	667
	A-1	1. NaH, THF, 0°; PhSeCl, -78° 2. H ₂ O ₂ (xs), NH ₄ Cl, CH ₂ Cl ₂ , 0°	I, R ¹ = H, R ² = OTBDMS (40)	704

Table XIC. α,β' -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

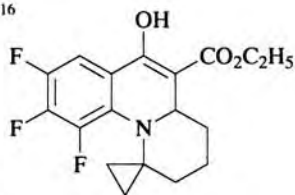

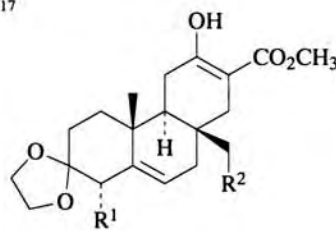
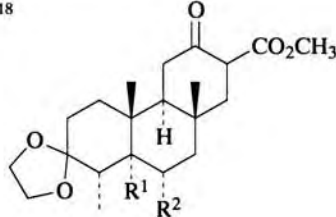
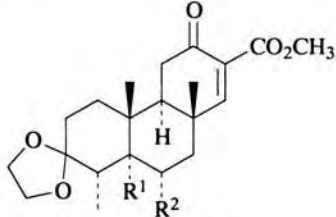
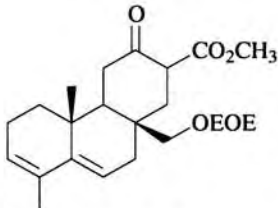
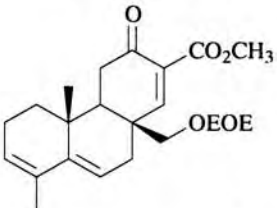
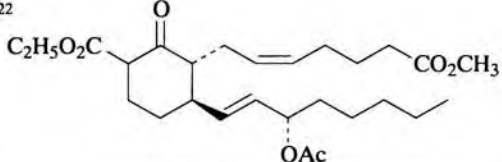
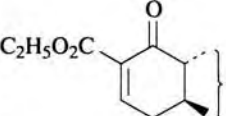
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₆ 	A-1	1. NaH, THF, 0 to 5°; PhSeCl, -78° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , rt	 (61)	705
C ₁₇ 	A-1	1. NaH, THF, rt; PhSeCl, 0° 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , Py, pH 7 (phosphate buffer)	I, R ¹ = H, R ² = OTBDMS (58)	330
	A-1	1. NaH, THF, 0° to rt; PhSeCl, 0° 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , 0°	I, R ¹ = CH ₃ , R ² = OEOE (67)	706

Table XIC. α,β' -Unsaturated β -Keto Esters, Acids, and Lactones (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₈ 	A-1	1. NaH, THF, rt; PhSeCl, 0° 2. H ₂ O ₂ (30%), Py, 0° to rt	 (84) R ¹ , R ² = double bond (84) R ¹ , R ² = epoxy (67)	707
	A-1	1. NaH, THF, -25 to 0°; PhSeCl 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°	 (73)	706
C ₂₂ 	A-1	1. NaH, THF, -25 to 0°; PhSeCl 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°	 (59) ^b	708

^a A 1:1 mixture of stereoisomeric selenides was obtained. One was oxidized, and the other was recycled to starting material.

^b The product was a mixture of keto and enol forms.

Table XIX. α,β^1 -Unsaturated β -Keto Amides, Lactams, and Nitriles

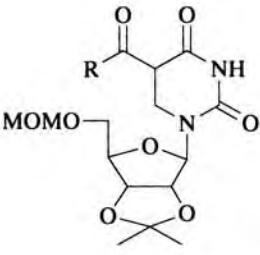
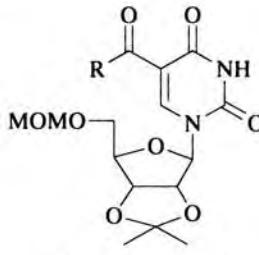
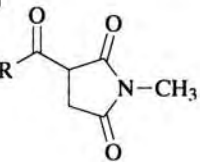
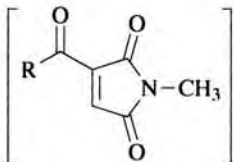
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, Py, CH ₂ Cl ₂ , 0° to rt, 24 h 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0°, 2 h	 R = C ₂ H ₅ (83) R = OC ₂ H ₅ (99) R = <i>i</i> -C ₃ H ₇ (88) R = <i>t</i> -C ₄ H ₉ (64) R = C ₆ H ₅ (90)	709, 290a
	A-1	1. NaH, THF, 0 to 20°; PhSeCl, 0 to 20° 2. MCPBA, CH ₂ Cl ₂ , Py, -15°	 R = C ₂ H ₅ (74) ^a (30) ^b (12) ^c R = <i>i</i> -C ₃ H ₇ (56) ^a (35) ^b (29) ^c R = C ₆ H ₅ (59) ^a (74) ^b (71) ^c R = <i>p</i> -ClC ₆ H ₄ (33) ^a (67) ^b (55) ^c R = <i>p</i> -CH ₃ OC ₆ H ₄ (28) ^a (64) ^b (52) ^c	172

Table XIX. α,β^1 -Unsaturated β -Keto Amides, Lactams, and Nitriles (Continued)

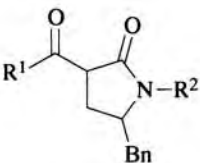




Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. NaH, THF, 0°; PhSeCl, -78° 2. MCPBA, CH ₂ Cl ₂ , -78 to 0°	I R ¹ = CH ₂ Cl, R ² = COC ₆ H ₅ (99) ^d	174
	A-1	1. LDA, THF, -75°, 15 min; PhSeCl, -75 to 0° (63) 2. MCPBA, CH ₂ Cl ₂ , 20°, 10 min	I R ¹ = C ₂ H ₅ , R ² = SO ₂ C ₆ H ₅ (94)	678
	A-1	1. LiN(TMS) ₂ , THF, -70°; PhSeCl (82) 2. H ₂ O ₂ (30%), MCPBA, CDCl ₃ , -50 to 0°	I R ¹ = (CH ₂) ₆ , R ² = COC ₆ H ₅ (40) ^d	173, 710
	A-1	(—)	I R ¹ = (CH ₂) ₁₀ , R ² = COC ₆ H ₅ (30)	173, 710a
	A-1	1. LiN(TMS) ₂ , PhSeCl 2. H ₂ O ₂ , MCPBA, -50 to 0°	I R ¹ = (CH ₂) ₄ , R ² = COC ₆ H ₅ (30) ^d	162
	A-1	1. LiN(TMS) ₂ ; PhSeCl (86) 2. H ₂ O ₂ , MCPBA	I R ¹ = (CH ₂) ₄ , R ² = COC ₆ H ₅ (30) ^d	162

Table XIX. α,β' -Unsaturated β -Keto Amides, Lactams, and Nitriles (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LiN(TMS) ₂ ; PhSeCl (95) 2. H ₂ O ₂ , MCPBA, -40°, 15 min; 0°	I R ¹ = R ² = COC ₆ H ₅ (38) ^d	201, 711
	A-1	1. LiN(TMS) ₂ ; PhSeCl -72°, (81) 2. H ₂ O ₂ , MCPBA, -15°, 15 min; 0°	I R ¹ = R ² = COC ₆ H ₅ (53) ^d	297
	A-1	1. LiN(TMS) ₂ , THF, -78°, (75) 2. H ₂ O ₂ , MCPBA, CDCl ₃ , -50, to 0°	I R ¹ = (CH ₂) ₆ R ² = COC ₆ H ₅ (52) ^d	536, 298
C ₂₄	A-1	1. LiN(TMS) ₂ , THF, -78°; PhSeCl (80) 2. H ₂ O ₂ , MCPBA, CHCl ₃ , -50°	 (34) ^d	203

Table XIX. α,β' -Unsaturated β -Keto Amides, Lactams, and Nitriles (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₂₇ C ₃₀	A-1	1. LiN(TMS) ₂ , THF, -70°; PhSeCl R = Ph (>78) R = indolyl (84) 2. H ₂ O ₂ , MCPBA, CDCl ₃ , -50, to 0°	 R = C ₆ H ₅ (58) R = (32) ^d	202, 712 713

^a The yield of selenide.^b The yield of Diels-Alder adduct with cyclopentadiene.^c The yield of Diels-Alder adduct with 2,4-hexadiene.^d The yield of Diels-Alder adduct.

Table XIE. α,β -Unsaturated Malonic Acids, Esters, Amides, and Nitriles

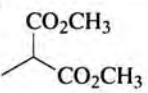
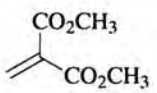
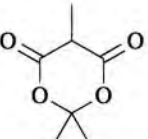
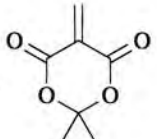
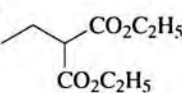
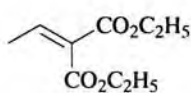
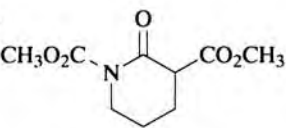
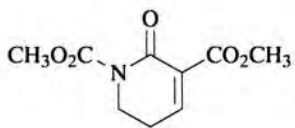
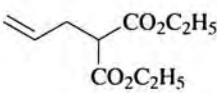
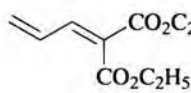
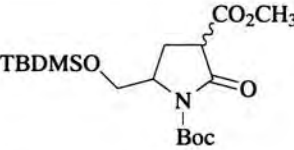
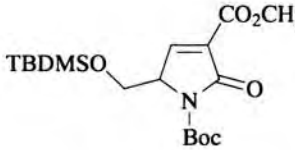
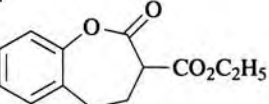
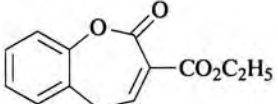
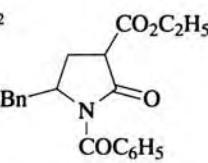
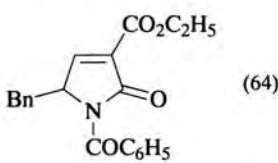
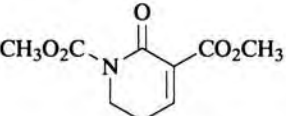
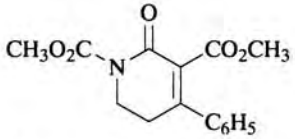
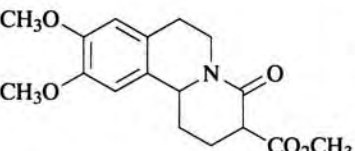
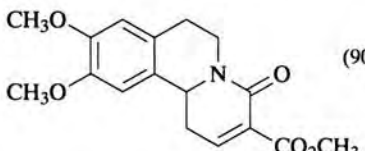
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₄ 	A-1	1. NaH (1.5 eq), THF; PhSeBr 2. H ₂ O ₂ (30%), CCl ₄ , 20°, 2 h	 (68)	714
	A-1	1. Sodium salt; PhSeBr, CH ₂ Cl ₂ , (67) 2. MCPBA (2.1 eq), CH ₂ Cl ₂ , -10°	 (53) ^a	176, 715
C ₅ 	A-6	1. NaH, HMPA (3 eq), THF, 0°; Se ⁰ , rt, 12-24 h MeI, 0°, 2 min (97) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0 to 25°, 15 min	 (98)	62
C ₆ 	A-1	1. NaH, THF, PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂	 (92)	716
	A-6	1. NaH, HMPA (3 eq), THF, 0°; Se ⁰ , rt, 12-24 h MeI, 0°, 2 min (78) 2. H ₂ O ₂ (30%), CH ₂ Cl ₂ , 0 to 25°, 15 min	 (96)	62

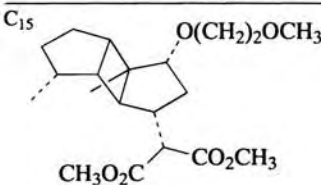
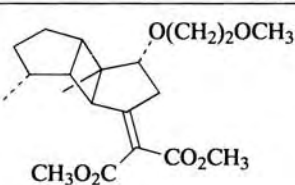
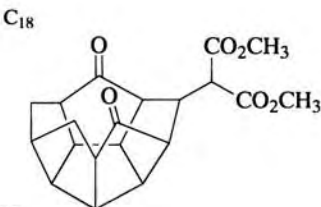
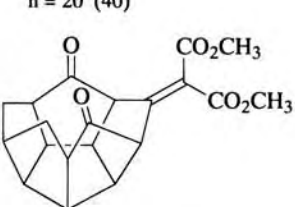
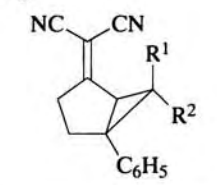
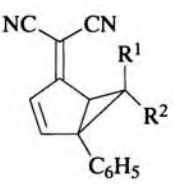
Table XIE. α,β -Unsaturated Malonic Acids, Esters, Amides, and Nitriles (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LiN(TMS) ₂ , THF; <i>n</i> -BuLi, -78°; PhSeCl (89) 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , 0°	 (95) ^b	717
C ₁₁ 	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂	 (>30)	718
C ₁₂ 	A-1	1. LDA, THF, HMPA, -78°; PhSeCl, -78 to 25° (84) 2. H ₂ O ₂ (15%), THF, AcOH, 0°	 (64)	719
	A-11	1. PhMgBr, CuBr•Me ₂ S, THF, HMPA; PhSeCl 2. H ₂ O ₂ , CH ₂ Cl ₂	 (40)	716
C ₁₄ 	A-1	1. NaH, C ₆ H ₆ /DMF (2:1), rt, 6 h; PhSeCl, rt, 1 h (90) 2. NaIO ₄ , NaHCO ₃ , MeOH/H ₂ O (8:1) rt, 30 min	 (90)	720, 396

270

271

Table XIE. α,β -Unsaturated Malonic Acids, Esters, Amides, and Nitriles (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
 C_{15}	A-1	1. NaH, THF; PhSeBr 2. H_2O_2 , CH_2Cl_2	 (99)	721
$\text{I}(\text{CH}_2)_n\text{CH}(\text{CN})_2$	A-1	1. $\text{KN}(\text{TMS})_2$, THF, -78° ; PhSeBr, -78 to 0° (63) 2. MCPBA, CH_2Cl_2 , 0°	$\text{I}(\text{CH}_2)_{n-1}\text{CH}=\text{C}(\text{CN})_2$ $n = 12$ (—) $n = 16$ (—) $n = 20$ (40)	722
 C_{18}	A-1	1. <i>n</i> -BuLi, C_6H_6 , 0° , 10 min; PhSeCl, rt, 30 min 2. H_2O_2 (30%), THF/EtOAc (1:1), 3 h	 (71)	179
 C_{21}	A-1	1. LDA, THF; -78° , 15 min; PhSeBr, THF, -78° , 5 min 2. H_2O_2 (15%), CH_2Cl_2 , Py, 25°	 $\text{R}^1 = \text{C}_6\text{H}_5$, $\text{R}^2 = \text{H}$ (46) $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{C}_6\text{H}_5$ (46) $\text{R}^1 = \text{R}^2 = \text{C}_6\text{H}_5$ (46)	228

^a The yield is that of the Diels-Alder adduct with cyclopentadiene.

^b No explanation was given for the double deprotonation.

Table XII. Aromatic Compounds

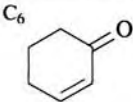
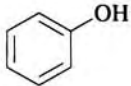
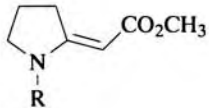
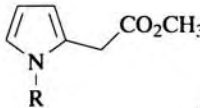
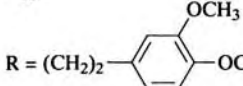
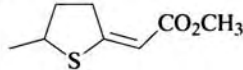
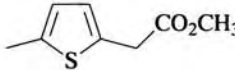
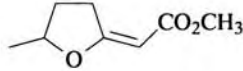
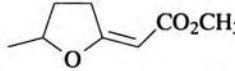
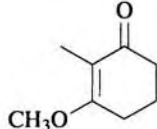
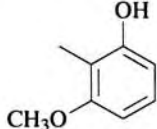
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-1	1. LDA, THF; -78°; PhSeCl 2. MCPBA, THF, -15° to rt	 (55)	723, 724
	A-1	1. LDA, THF; -78 to 0°; PhSeBr, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, rt	 R = (CH ₂) ₂ -  (86) R = (CH ₂) ₅ CO ₂ CH ₃ (71)	227
	A-1	1. LDA, THF; -78 to 0°; PhSeBr, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, rt	 (95)	227
	A-1	1. LDA, THF; -78 to 0°; PhSeBr, -78 to 0° 2. H ₂ O ₂ (30%), THF, AcOH, rt	 (94)	227
	A-1	1. LDA (2.2 eq); PhSeBr, (2.2 eq) (45) 2. MCPBA, -25°, CH ₂ Cl ₂ ; 3,5-dimethoxyaniline, 20°	 (73)	218

Table XII. Aromatic Compounds (Continued)

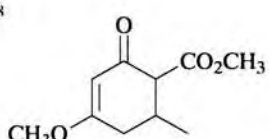
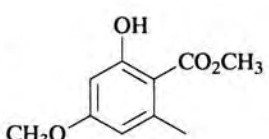
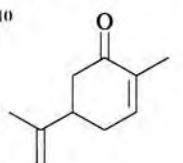
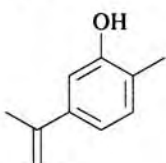
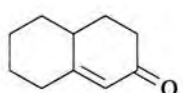
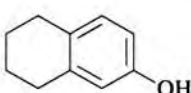
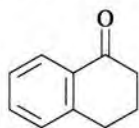
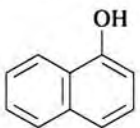
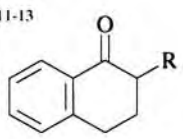
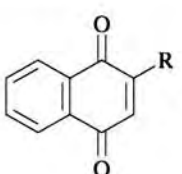
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₈ 	A-1	1. LDA, THF, -60 to -70°, 15 min; PhSeBr, -45° 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°; rt, 2 h	 (84)	725
C ₁₀ 	A-1	1. LDA, THF, -78°; PhSeCl 2. H ₂ O ₂ , THF, -15°	 (10)	724
	A-1	1. LDA, THF, -78°; PhSeCl 2. MCPBA (2 eq)	 (50)	724
	B-3	1. PhSeCl ₃ (0.5 eq), Et ₂ O, 0°, 20 min; SOCl ₂ (94) 2. NaHCO ₃ , H ₂ O, CH ₂ Cl ₂ , rt, 4 h	 (52)	382, 72
C ₁₁₋₁₃ 	B-2	1. (PhSeO) ₂ O, AlCl ₃ , heat	 R = CH ₃ (51) R = C ₂ H ₅ (51) R = <i>i</i> -C ₃ H ₇ (24)	284

Table XII. Aromatic Compounds (Continued)

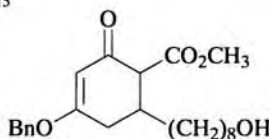
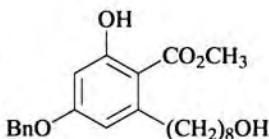
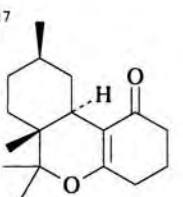
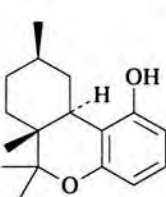
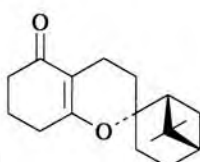
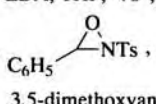
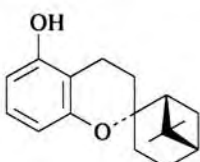
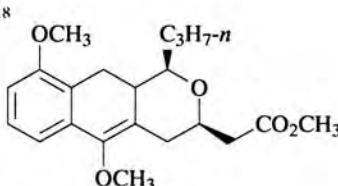
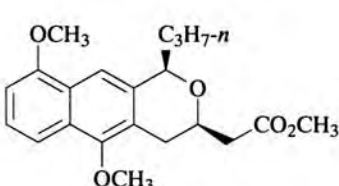
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₁₅ 	A-1	1. LDA, THF, -60 to -70°, 15 min; PhSeBr 2. H ₂ O ₂ (15%), CH ₂ Cl ₂ , Py, 0°; rt, 2 h	 (>70)	298a
C ₁₇ 	A-1	1. LDA (2.2 eq); PhSeBr, (2.2 eq) (76) 2. MCPBA, -25 to -35°, CH ₂ Cl ₂ ; 3,5-dimethoxyaniline, 20°	 (66)	218
	A-1	1. LDA, THF, -78°; PhSeCl (62) 2.  , 3,5-dimethoxyaniline	 (46)	213
C ₁₈ 	A-3	1. PhSeBr, AgO ₂ CCF ₃ , C ₆ H ₆ (74) 2. O ₃ , -78°, CH ₂ Cl ₂ ; 25°	 (64)	726

Table XII. Aromatic Compounds (*Continued*)

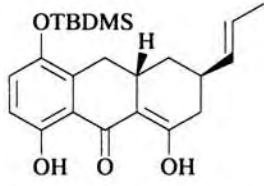
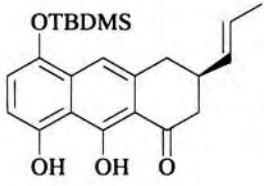
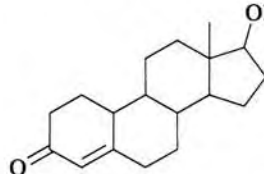
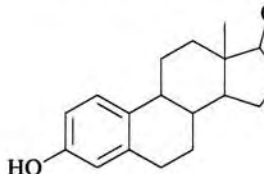
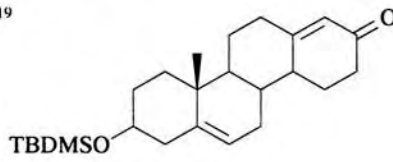
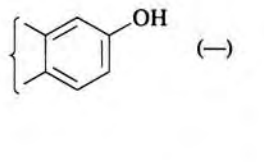
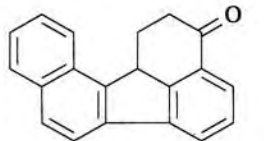
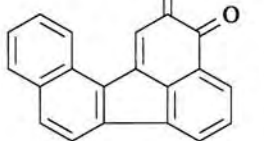
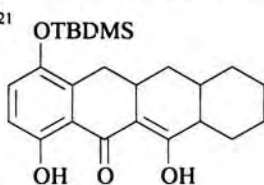
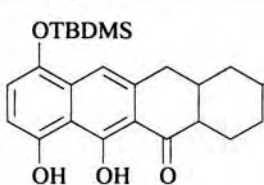
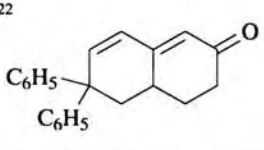
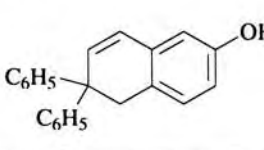
Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, Py, 0° 2. H ₂ O ₂ (30%)	 (—)	262
	A-1	1. LDA (2 eq), THF, -78°; PhSeCl 2. H ₂ O ₂ (3.5 eq), THF, -15°	 (52)	724
	A-1	1. LDA; PhSeCl 2. [Ox]	 (—)	727
	A-2	1. PhSeCl, EtOAc, (84) 2. H ₂ O ₂ , NaOH, EtOAc, THF	 (40) ^a	728

Table XII. Aromatic Compounds (*Continued*)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
	A-2	1. PhSeCl, Py, 0° 2. H ₂ O ₂ (30%)	 (—)	262
	A-1	1. LDA, THF, -78°; PhSeBr (58) 2. H ₂ O ₂ , H ₂ O, CH ₂ Cl ₂ , 0° to rt	 (69)	729

^a The dione was presumably formed by further oxidation of the enone.

Table XIII. Miscellaneous

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_3 	A-1	1. NaH, THF, 0°; PhSeCl, 1 min 2. H2O2 (15%), CH2Cl2, 0 to 25°	(82)	730
	D-1	MCPBA	(70-80)	731
$R^1SO_2CH_2CO_2R^2$	A-1	1. NaH, THF, -10°, 2 h; PhSeBr, -20° to rt 2. H2O2, CH2Cl2, 0°		732
		<u>Selenide yield</u>		
		R ¹ = CH ₃ , R ² = <i>t</i> -C ₄ H ₉	(75) (75-99)	
		R ¹ = <i>t</i> -C ₄ H ₉ , R ² = CH ₃	(80) (75-99)	
		R ¹ = R ² = <i>t</i> -C ₄ H ₉	(98) (99)	
C_4 	A-1	1. NaH, THF, 60°, 1 h; PhSeBr, -75° to rt (90) 2. H2O2 (30%), CH2Cl2, -10 to 0°, 3 h	(78)	733
	A-1	1. NaH; PhSeBr (65) 2. H2O2 (30%)		
			R = (CH ₂) ₂ TMS (83)	734
			R = <i>t</i> -C ₄ H ₉ (—)	735

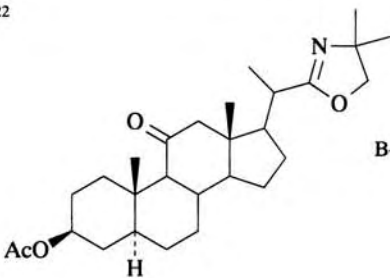
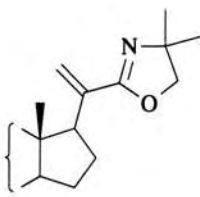
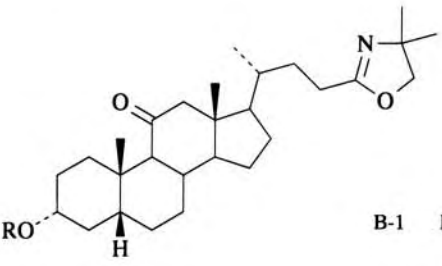
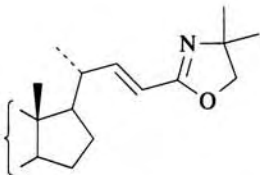
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Table XIII. Miscellaneous (Continued)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C_7 	B-1	PhSeO ₂ H, Py, C ₆ H ₆ , 80°, 1 h, H ₂ O removal	(92)	90
C_{10} 	A-1	1. NaH, THF, 0°; PhSeCl, 0° (78) 2. H2O2 (15%, 2 eq), CH2Cl2, Py	(71)	2
C_{15} 	A-1	1. LDA, THF, -78°; PhSeCl (61) 2. MCPBA (1.2 eq)	(52)	678
	B-2	PhSeO ₂ H, Py, C ₆ H ₆ , 80°, 2 h, H ₂ O removal	(85)	90

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Table XIII. Miscellaneous (*Continued*)

Substrate	Method (Table I)	Conditions for Selenenylation (% Yield) and Oxidation	Product(s) and Yield(s) (%)	Refs.
C ₂₂ 	B-1	PhSeO ₂ H, Py, C ₆ H ₆ , 80°, 6 h, H ₂ O removal	 (81)	90
C ₂₄ 	B-1	PhSeO ₂ H, Py, THF, 60°, 1 h, (33) H ₂ O ₂ , rt, 20 min	 I R = H (100)	90
	B-1	PhSeO ₂ H, Py, 60°, 6 h	I R = Ac (100)	90

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