Ketene Cycloadditions

John A. Hyatt, Eastman Chemical Co., Kingsport, Tennessee
Peter W. Raynolds, Eastman Chemical Co., Kingsport, Tennessee

1. Introduction

The reaction of ketene with itself was described almost simultaneously in 1908 by Chick and Wilsmore in England, (1) and by Staudinger and Klever in Germany; (2) priority for the discovery was attributed to Wilsmore by the German group. (3)

Ketene cycloaddition was an early example (along with the Claisen, Diels-Alder, and ene reactions) of a peculiar process, one that formed carbon–carbon bonds with ease, often without the need for solvent, catalyst, or high heat. Subsequent work by others was done in the shadow of Staudinger's exhaustive and rigorous study of all phases of ketene reactivity. (4) Three factors led to a resurgence of interest in this reaction beginning in the 1960s. Haloketenes, which had previously eluded study, were found to have high reactivity, and the halogens could easily be removed after the reaction. (5-7) The increasing sophistication of powerful analytical methods, particularly nuclear magnetic resonance spectroscopy, led to discovery of the interesting stereochemical aspects of this reaction. Finally, the new theory of orbital symmetry conservation provided a conceptual framework to rationalize these puzzling “no mechanism” reactions. (8)

This is a review of cycloaddition reactions of ketenes. Here, a cycloaddition is defined as a reaction of a ketene with an unsaturated organic compound to give a cyclic product by a mechanism that, in principle, involves the almost simultaneous formation of two bonds between two reactants. While we are indifferent to whether bond formation is concerted or stepwise, no other chemical process can take place between the formation of the first and second bond. Our definition involves both structural and mechanistic factors, and it was difficult to avoid a certain amount of arbitrariness. We exclude products, such as dehydroacetic acid, which seem to us to arise by concatenation of ketene molecules followed by cyclization. These reactions, in our view, are more properly considered to arise from a series of ionic reactions, and the prediction of the eventual product does not take advantage of the special mechanistic features commonly associated with true cycloadditions. Additions to imines to give β -lactams are numerous and will be covered in a separate review. The literature has been searched to the end of 1988.

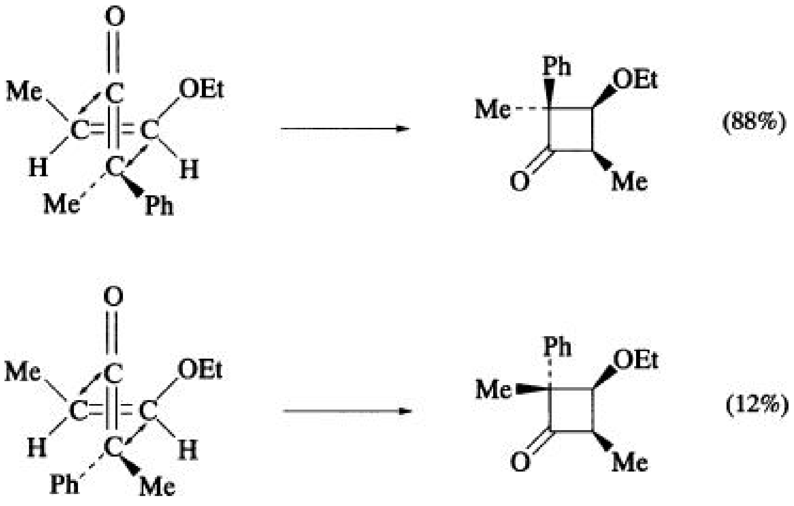
Many reviews devoted partially or exclusively to ketene cycloadditions have been published. (4, 9-18) Specific topics that have been reviewed include haloketenes, (19, 20) fluoroketenes, (21, 22) cyanoketenes, (23) intramolecular cycloadditions, (24, 25) conjugated ketenes, (26) and β -lactam antibiotics. (27, 28) Ancillary topics pertinent to ketene cycloadditions that have been reviewed include cycloreversion reactions, (29) ketene equivalents, which provide ketene functionality with olefin-like reactivity especially in [4 + 2] reactions, (30) application of frontier molecular orbital theory to cycloadditions, (31) and a critical discussion of cycloadditions with polar intermediates. (32) Applications of cyclobutanones in synthesis have also been reviewed. (33-35)

2. Mechanism and Stereochemistry

Ketene cycloadditions resemble certain other processes, such as the Cope rearrangement and the Diels-Alder, Claisen, and ene reactions, in that carbon–carbon bond formation occurs readily, even in the absence of catalyst, solvent, light, or high heat. Features of ketene cycloadditions that were difficult to rationalize with the mechanistic knowledge available at the middle of the twentieth century included the formation of a four-membered ring by a nonphotochemical process, even when, in the case of 1,3-dienes, a cyclohexene was possible; (36) the retention of stereochemistry about the olefin in the cyclobutanone product; the fact that *cis*-alkenes reacted much faster than *trans*-alkenes, (37) and that monosubstituted ketenes reacted with cyclopentadiene to put the substituent in the *endo* position of the bicyclo[3.2.0]hept-2-en-7-one. (38) When the concept of orbital symmetry conservation proved so useful in explaining many processes of this type, (39) it became natural to view ketene cycloadditions as one example of this general phenomenon. Much of the mechanistic research that has been conducted on ketene cycloadditions since then has focused on the timing of bond formation and other features of the reaction that would tend to support or disprove the orbital symmetry conservation theory. While such work was of great importance as the practical limits of symmetry conservation theory were explored, it had the potential to disguise the fact that most of the special features of ketene cycloadditions arise from the geometry of approach of the two reactants, and that the “orthogonal” mode of attack does not require symmetry theory. (40, 41)

2.1.1.1. Geometry of Approach

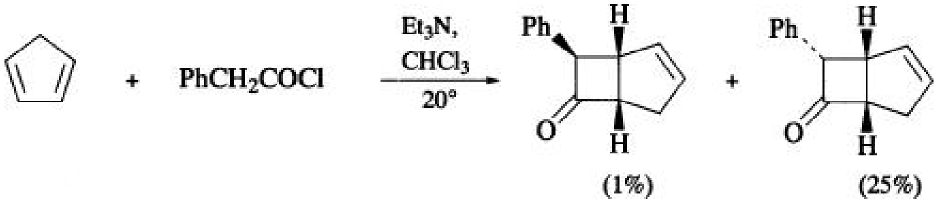
The hallmark of ketene cycloaddition is the peculiar way that the two reactants approach each other. Rather than lining up in parallel fashion before forming bonds, the ketene and olefin come together at right angles, in what is termed an “orthogonal” approach. (37, 38, 42) This arrangement produces an unusual result: the bulkiest substituent on the ketene ends up on the most sterically hindered face of the cyclobutanone (Eq. 1). The larger the difference in bulk of the two substituents on the ketene, the larger the effect. In the nomenclature devised by Woodward and Hoffmann, (39) the ketene forms bonds antarafacially (on different sides of the π bond), while the olefin forms bonds suprafacially (on the same side of the π bond). It should be noted that while this unusual geometry is well explained by symmetry conservation theory, the same



(1)

geometry can occur with a dipolar intermediate as well. (43, 44) This geometry immediately suggested explanations for the higher reactivity of *cis*-over *trans*-alkenes, and the fact that one substituent on the ketene or alkene often accelerates cycloaddition, possibly because of electronic effects, while two substituents on one of the reactants results in a rate reduction, presumably because of steric effects. (37, 45)

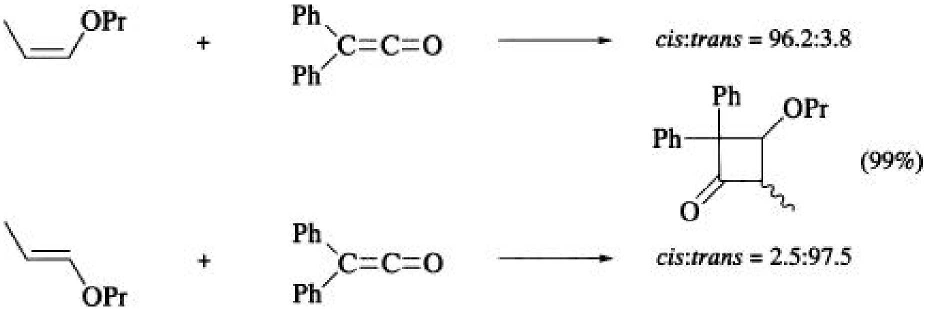
The antarafacial involvement of the ketene was first noted in the addition of ketenes to cyclopentadiene. The larger substituent on the ketene tends to end up in the *endo* position, on the concave face of the bicyclo[3.2.0]hept-2-en-6-one. (38) This so-called “*endo* effect” is common with cyclic olefins, but the source of the selectivity may be due to a combination of factors. Equilibration experiments showed that most substituents are slightly more stable in the 7-*endo* position than in the 7-*exo* position of a bicyclo[3.2.1]heptane. (46) For example, at equilibrium, the *endo/exo* ratio for a 7-phenyl group in the product of Eq. 2 is 66/34. Thus the *endo* position is the more stable, but the thermodynamics of the product do not explain all of the selectivity.



(2)

2.1.1.2. Retention of Stereochemistry

Stereochemistry about the olefin is retained in the cyclobutanone product. Slight (<5%) stereochemical leakage has been noted in the reaction of diphenylketene with propenyl propyl ether (Eq. 3). (47) This result lends credence to, rather than weakens, the general conclusion that significant loss of stereochemistry is not to be expected in any except the most polar systems.



(3)

2.1.1.3. Solvent Effects

The rate of cycloaddition increases as the polarity of the solvent is increased. (48) Dimethylketene dimerizes 19 times faster in acetonitrile than in hexane. (49) This result is all the more noteworthy because if bond formation were completely synchronous, the reaction should have shown an inverse solvent effect, or a rate retardation with increasing solvent polarity, since the reactant has a larger dipole moment than the product. Solvent effects, while general, are not always of practical importance, since ketene cycloadditions are generally run without solvent if possible. The effect of a polar solvent on rate is often negated by dilution of the reactants. If two products can form, the ratio often depends on the polarity of the solvent. This effect is most important with more highly reactive polar systems.

2.1.1.4. Substituent Effects

As mentioned above, one substituent on either the ketene or the olefin generally accelerates the reaction, while two generally slow the reaction because of steric effects. This result can be rationalized by the geometry of approach: one bulky substituent can position itself away from the reaction center, causing little change in rate from steric effects, while a second substituent is placed in the immediate vicinity of the other reactant. The rate of cycloaddition is accelerated by electron-donating substituents on the olefin and by electron-withdrawing groups on the ketene.

2.1.1.5. Timing of Bond Formation

Both solvent and isotope effects on the rate of dimethylketene dimerization (50-54) indicate that cycloaddition of even relatively symmetrical reactants occurs with at least some nonsynchronous character. In more polar systems, such as cycloadditions of *tert*-butylcyanoketene, it is difficult to avoid explanations involving stepwise mechanisms with a dipolar intermediate. (55) Recent theoretical *ab initio* calculations do not support a concerted, supra-antarafacial mechanism for the addition of ketene to ethylene. (56)

Nevertheless, alkenes without electron-donating groups cycloadd in a way that seems to allow no alternative reaction pathway between the formation of the first and second bonds, if indeed the two bonds are not formed at almost the same time. Bond rotation resulting in loss of stereochemistry does not occur, as illustrated in the impressive addition of diphenylketene to *trans*-cyclooctene with no loss of stereochemistry. (57) As exemplified in Table IV, addition to anti-Bredt olefins takes place in high yield; side reactions resulting from a charged intermediate are exceptional.

2.1.1.6. Reversibility

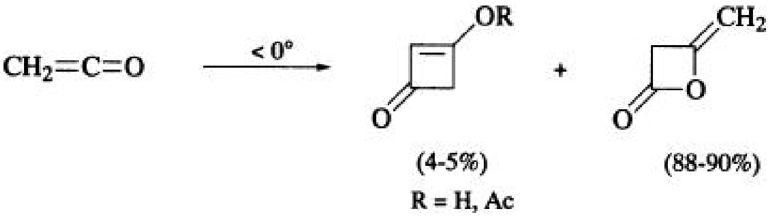
The formation of simple cyclobutanones is reversible under relatively mild conditions. For instance, 2,2,3-triphenylcyclobutanone gives diphenylketene and styrene upon pyrolysis at 200°, while the same compound cleaves to triphenylethene and presumably ketene upon photolysis. (58)

3. Scope and Limitations

3.1. [2 + 2] Cycloadditions

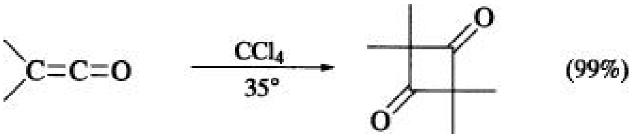
3.1.1.1. Dimerization

The dimerization of ketenes gives 1,3-cyclobutanediones and β -propiolactones. Higher oligomers which likely arise from secondary reactions are also obtained. If the cyclobutanedione has an acidic hydrogen, the enol form generally predominates, and acylation of the enol may occur. Ketene, which can be handled as the pure, colorless liquid at –78°, dimerizes exothermically below room temperature to afford mostly the β -propiolactone (Eq. 4). The highly reactive unsubstituted diketene, which is prepared on a multimillion pound per year scale by the pyrolysis of acetic acid, is an industrially important raw material used in the preparation of acetoacetates and acetoacetamides. (59)



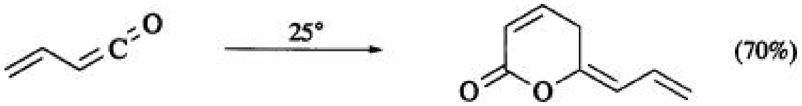
(4)

Disubstituted ketenes, except those with electron-withdrawing groups, give 1,3-cyclobutanediones in very high yield, as exemplified by the dimerization of dimethylketene (Eq. 5). (49) The reaction rate is sensitive to the polarity of the solvent, (49) as well as to the electronic and steric nature of the substituents. For instance, dimethylketene is highly reactive at room temperature, whereas diphenyl- and ethylbutylketene are stable enough to be stored at room temperature for months without appreciable degradation.



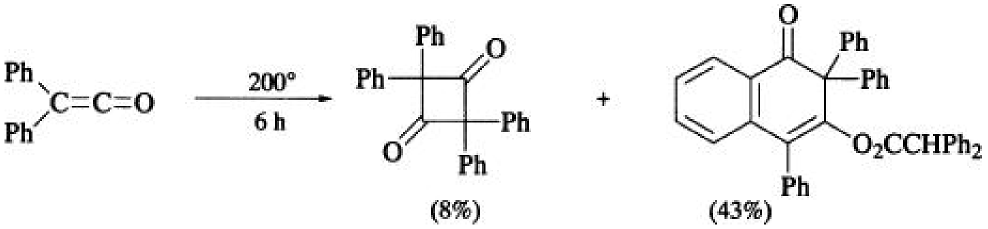
(5)

A double bond in conjugation with the ketene can participate in the dimerization, either initially, as in the case of vinylketene (Eq. 6), (60) or in what could be a



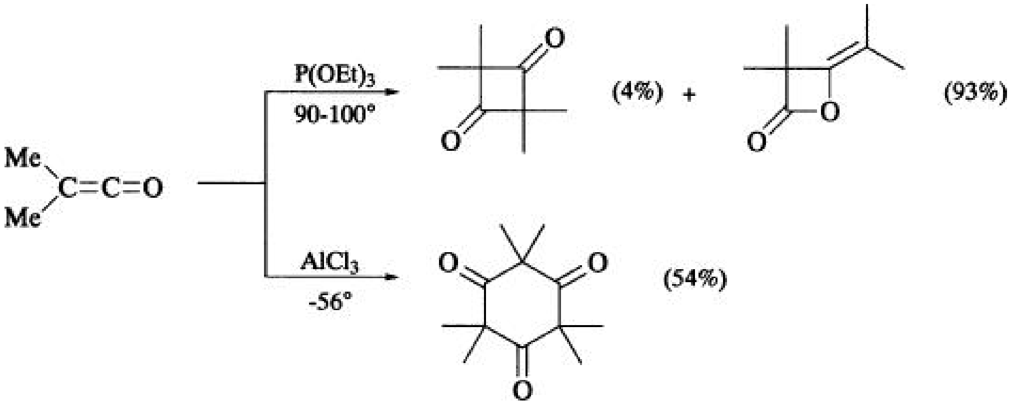
(6)

rearrangement of the primary dimerization product of diphenylketene (Eq. 7). The cyclobutanedione is the only product observed at lower temperatures. (61)



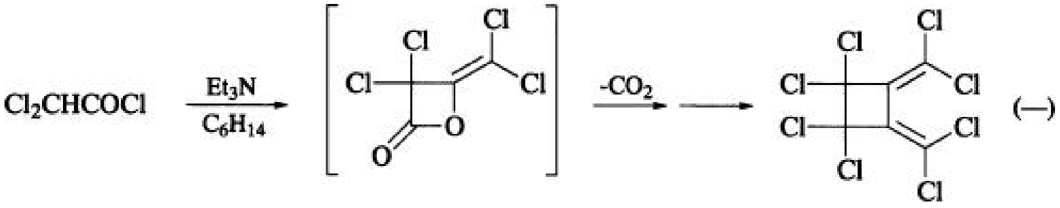
(7)

Lewis acids such as aluminum chloride, (62) and bases such as triethyl phosphite, (48) alter the course of the uncatalyzed dimerization, and other products, probably arising from ionic processes, are formed (Eq. 8).



(8)

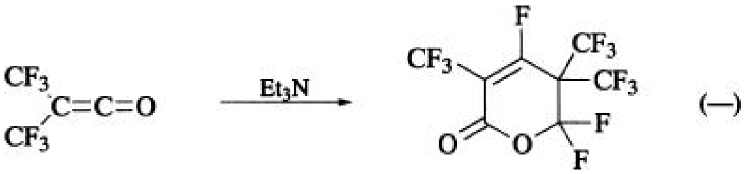
Disubstituted ketenes with at least one electron-withdrawing group behave differently. A dimer of dichloroketene has not been described, although in one instance, a secondary product, possibly derived from a β -propiolactone dimer, was isolated (Eq. 9). (63)



(9)

A solution of dichloroketene in octane, distilled from a mixture of trichloroacetyl bromide and zinc, was stable for a week at room temperature or for 24 hours at 85°; no evidence for a dimer was found in the IR spectrum of the mixture. (7)

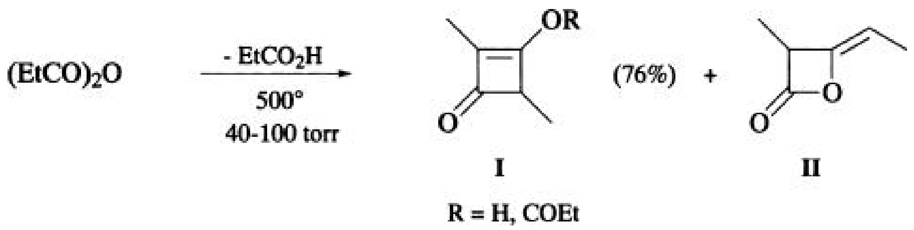
Bis(trifluoromethyl)ketene likewise does not dimerize thermally (64, 65) but affords the β -propiolactone dimer with diethyl nitroxide. (66) A γ -lactone is obtained in the presence of triethylamine (Eq. 10). (67)



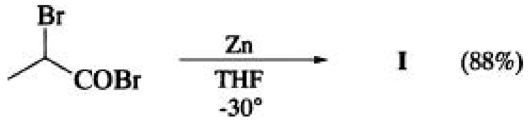
(10)

Spontaneous dimerization is not observed with *tert*-butylcyanoketene, while the β -propiolactone dimer is obtained in the presence of triethylamine. (68) No dimer was reported for *tert*-butylcarboethoxyketene after 2 months at room temperature. (69) Various products are obtained from ketenes bearing one electron-withdrawing group and a second substituent less bulky than *tert*-butyl, as indicated in Table II.

Monosubstituted ketenes, like ketene itself, give mixtures of hydroxycyclobutenone (the enol form of the 1,3-cyclobutanedione product, which is often acylated), and the β -propiolactone. Although exceptions exist, it appears that the hydroxycyclobutenone is most likely to be formed under salt-free conditions [pyrolysis of an anhydride, or zinc dechlorination followed by distillation, (Eqs. 11 and 12)], while dehydrochlorination of an acid chloride with triethylamine almost always yields the lactone (Eq. 13).



(11)

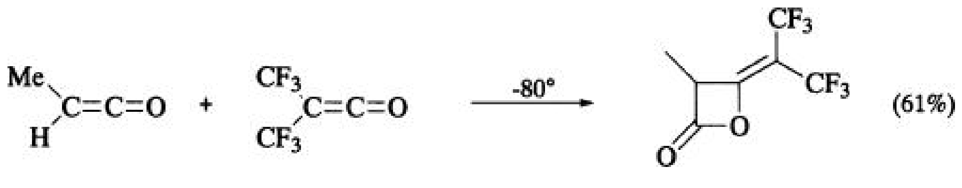


(12)

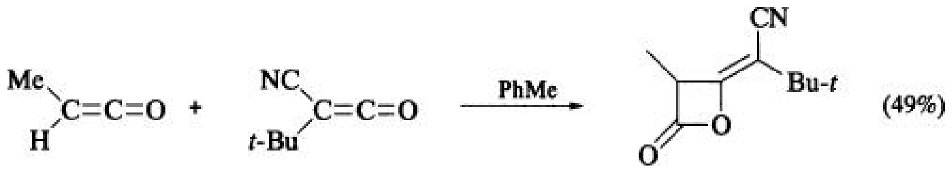
(13)

Monoalkylketenes are much more reactive than either the unsubstituted or disubstituted species and, except in sterically hindered examples, dimerization occurs below 0°. They are generally not dealt with as pure compounds but rather are treated as transient species in solution below 0°. Trimethylsilylketene, which does not dimerize, is a noteworthy exception. (70)

Mixtures of unlike ketenes can produce unsymmetrical products in synthetically useful yields, especially when the electronic characteristics of the two reactants are different. Ketene and monosubstituted ketenes react with electron-poor ketenes to give β -propiolactones, with the oxygen of the electron-poor ketene becoming the lactone oxygen (Eqs. 14 and 15). (64, 71, 72)

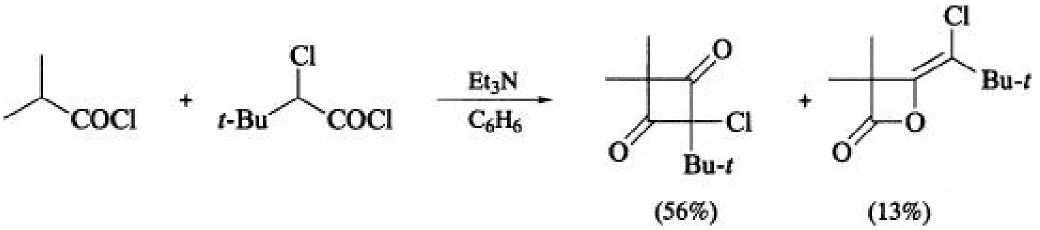


(14)



(15)

Disubstituted ketenes react with other disubstituted ketenes to give predominately 1,3-cyclobutanediones, but, in contrast to homodimerizations, the β -propiolactone product is sometimes observed (Eq. 16). (73)



(16)

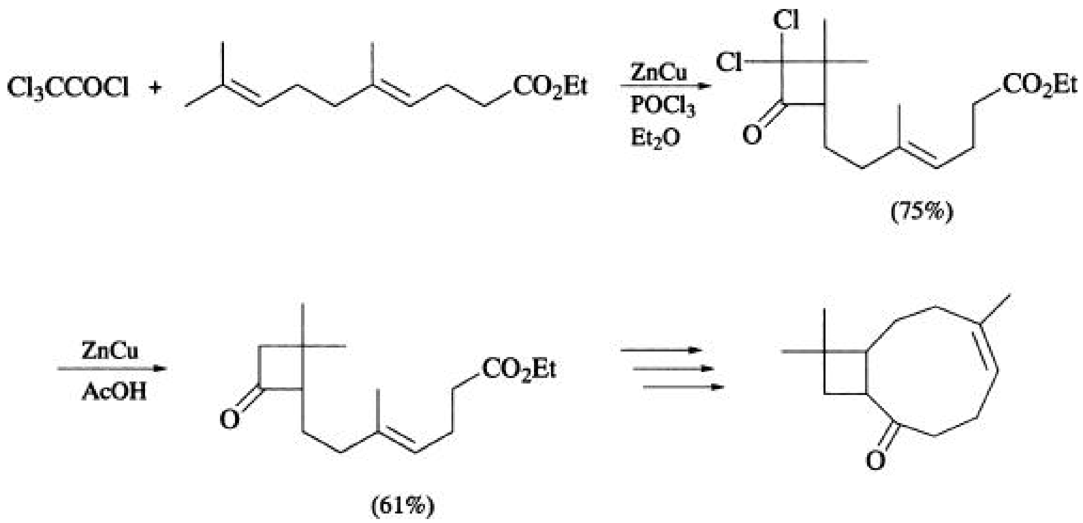
Cyclobutanedione dimers of unsubstituted and disubstituted ketenes are efficiently converted into the ketenes by pyrolysis in a hot tube. (74) If the dimer is available, thermal cycloreversion is often the best preparative method for the ketene. However, this method has not been extended to the less well studied monosubstituted ketenes.

3.1.1.2. Isolated Olefins

Ketenes react with simple alkenes to afford, in almost all cases, cyclobutanones. In the absence of electron-donating substituents, the order of reactivity is *trans* olefin < *cis* olefin < cyclic olefin < linear diene < cyclic diene. (37) The stereochemistry about the double bond is retained, even in the extreme case of cycloadditions to *trans*-cyclooctene (Eq. 17). (57)

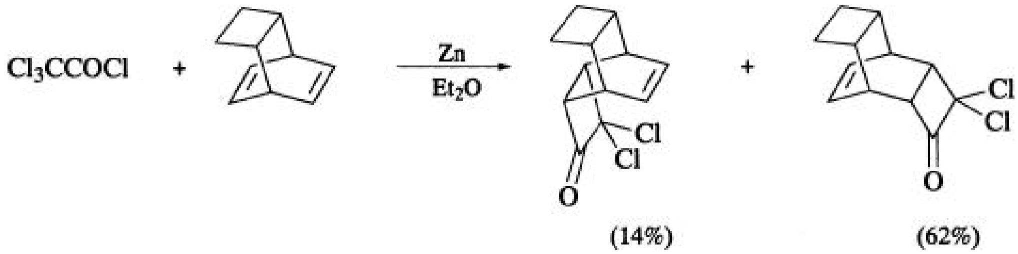
(17)

Regiochemistry is determined by the polarization of the double bond, even in the face of steric crowding by substituents on the 2 and 3 positions of the cyclobutanone. Except when the ketene is activated by electron-donating or withdrawing substituents, useful yields are obtained only when the ketene is disubstituted. Should the cycloaddition product of ketene itself be desired, it is common to use the highly reactive dichloroketene followed by dechlorination with zinc-copper, as in the synthesis of isocaryophyllene (Eq. 18). (75)



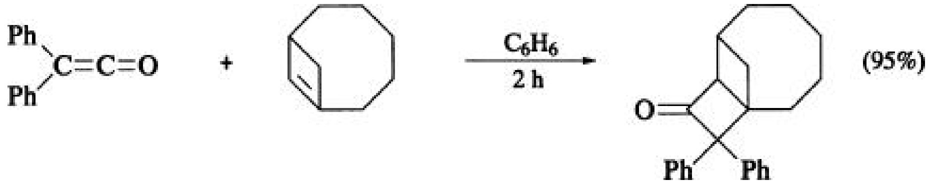
(18)

If the substrate contains two unsaturated centers, reaction at both sites is often observed (Eq. 19). (76)

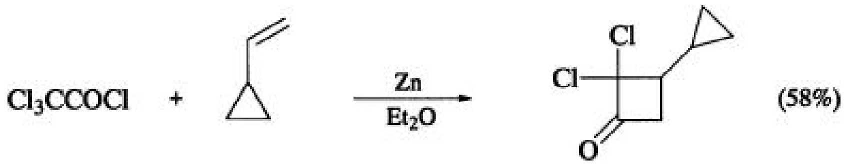


(19)

Side reactions are not common if the substrate does not contain an activating group. No rearrangement was seen with an “anti-Bredt” olefin, (77) or with a reactant prone to cyclopropylcarbinyl carbenium ion rearrangement (Eqs. 20 and 21). (78)

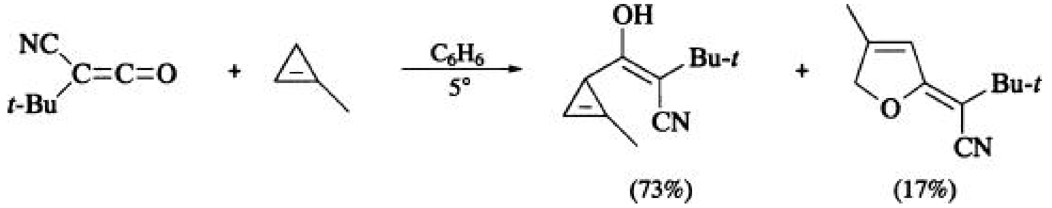


(20)



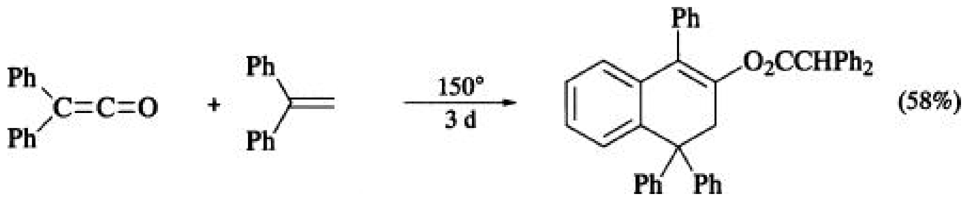
(21)

On the other hand, methylcyclopropene gives ene-type and rearranged products, possibly by way of dipolar intermediates (Eq. 22). (79)



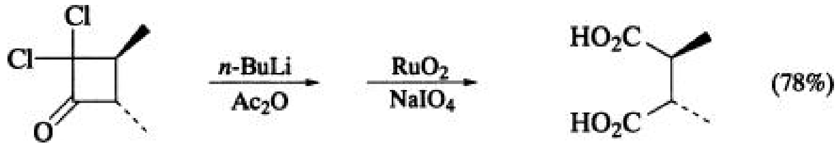
(22)

Diphenylketene gives a 2:1 adduct with 1,1-diphenylethene (Eq. 23). (80, 81) The cyclobutanone is not observed.



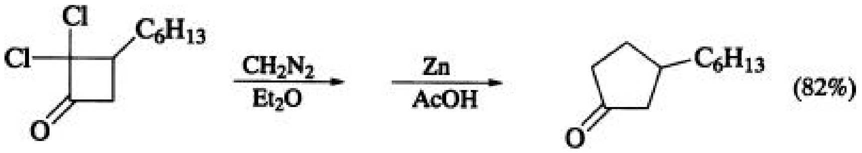
(23)

Dichloroketene adducts can be converted to useful derivatives. Sequential treatment with *n*-butyllithium and acetic anhydride followed by oxidation with ruthenium dioxide and sodium metaperiodate affords vicinal dicarboxylic acids stereospecifically (Eq. 24). (82)



(24)

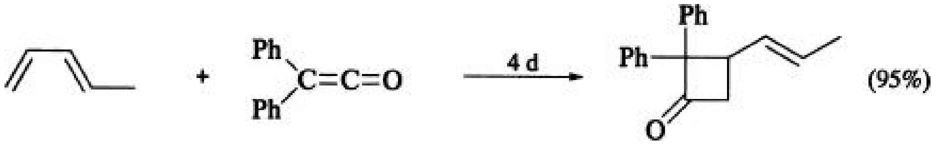
A three-carbon annelation sequence, involving methylene insertion with diazomethane followed by removal of the chlorines, affords cyclopentanones (Eq. 25). (83)



(25)

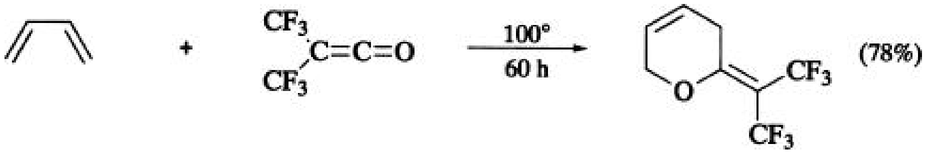
3.1.1.3. Linear Dienes

The reaction of ketenes with unpolarized acyclic dienes gives cyclobutanones. Although formation of cyclobutanones instead of Diels–Alder adducts is one of the characteristics of ketene cycloadditions (Eq. 26), cyclic

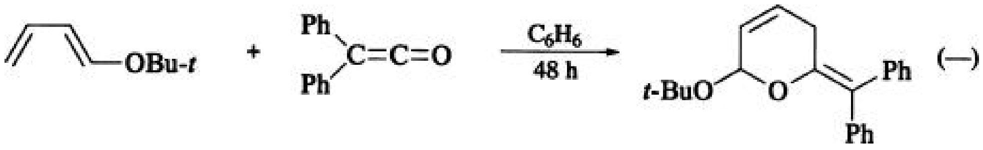


(26)

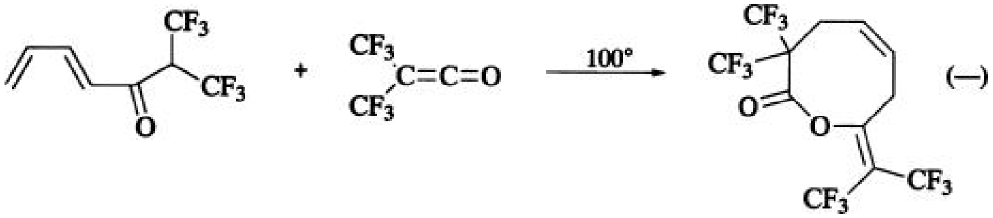
products with larger rings, often arising from addition across the ketene carbonyl, are common with perfluoroketenes (84, 85) (Eqs. 27 and 29) or with alkoxybutadienes (Eq. 28). (86) The reaction of ketene with 1,3-butadiene has been reported, (87)



(27)



(28)



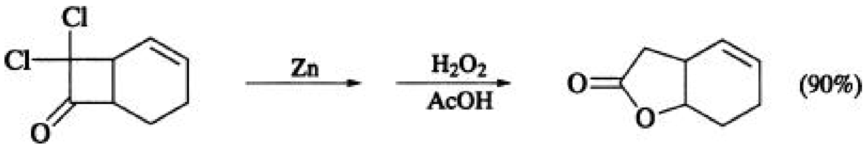
(29)

but useful yields of cyclobutanones are generally obtained only when the ketene has two substituents. (36)

3.1.1.4. Cyclic Dienes

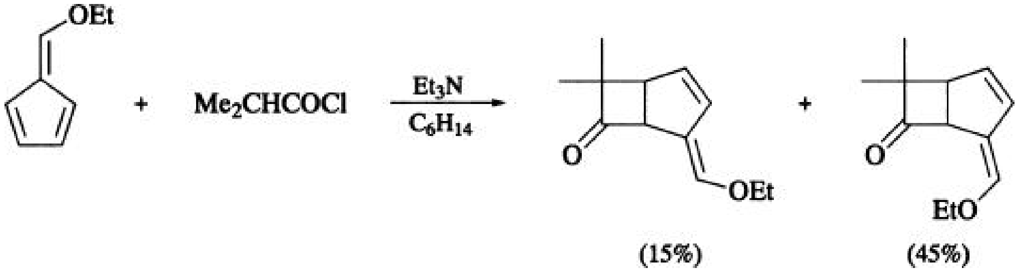
As discussed in the Mechanism section, cyclic dienes react with ketenes to yield cyclobutanones. The larger of the two substituents on the ketene goes in the *endo* position.

Dehalogenation of the dichloroketene adduct to various cyclic dienes, followed by oxidation, affords a simple route to key intermediates in the synthesis of prostaglandins (Eq. 30). (88-91)



(30)

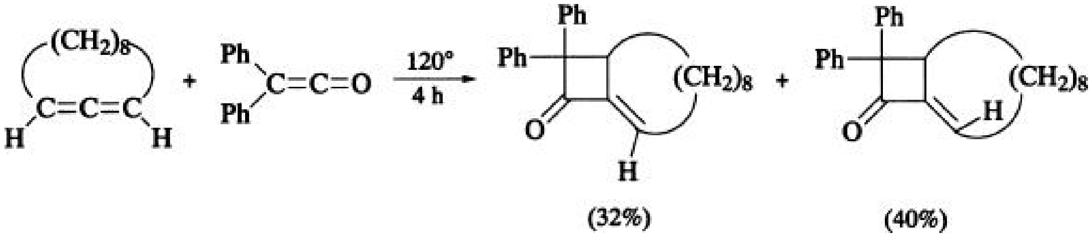
Most fulvenes react on the ring (Eq. 31.) (92)



(31)

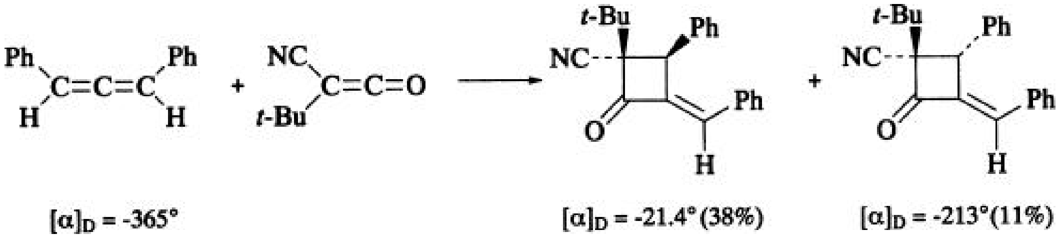
3.1.1.5. Allenes

Addition of ketenes to allenes yields methylenecyclobutanones. If the allene is unsymmetrical, all possible products are often formed, and there are no simple rules to predict which will predominate. The 1,3-disubstituted allenes can react to put the substituent on the methylene in a position either *Z* or *E* to the carbonyl, and both products are often observed (Eq. 32). (93) Acyclic 1,3-dialkylallenes



(32)

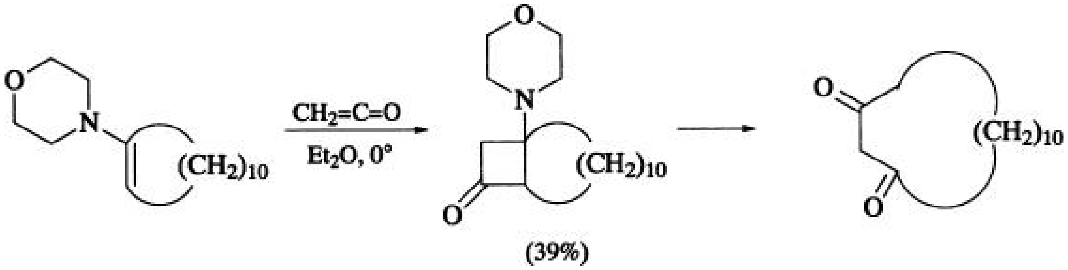
usually give more *Z* than *E* isomer, (93) and, since the optical activity of chiral allenes is mostly lost in the *Z* isomer, it has been argued by some that this reaction occurs by a stepwise mechanism. (94) On the other hand, optically enriched 1,3-diphenylallene affords only the two *E* isomers, which are optically active (Eq. 33). (95)



(33)

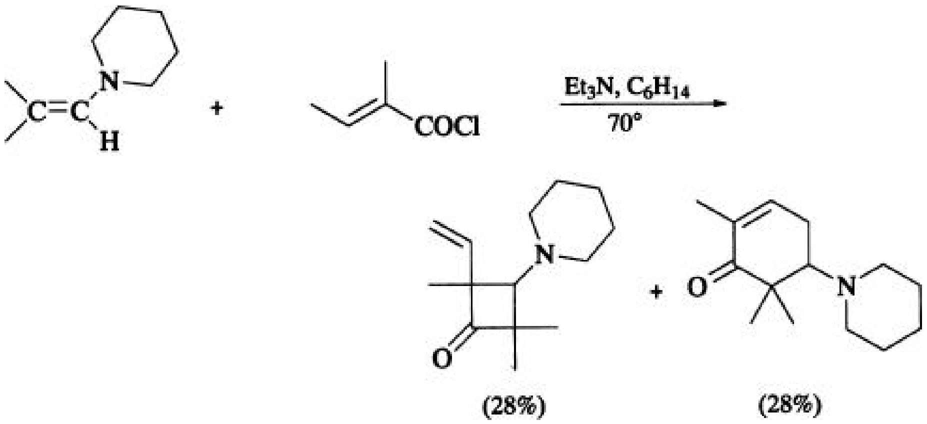
3.1.1.6. Enamines

Enamines react readily with ketenes. When the enamine nitrogen atom bears two alkyl substituents, the cyclobutanone product is, in many cases, not isolated in a synthetically useful yield. Part of the reason for the relatively few examples of isolated [2 + 2] adducts may be that rearrangement of the intially formed cyclobutanone is often the desired outcome of the sequence, as in the preparation of 1,3-cyclotetradecanedione (Eq. 34). (96)



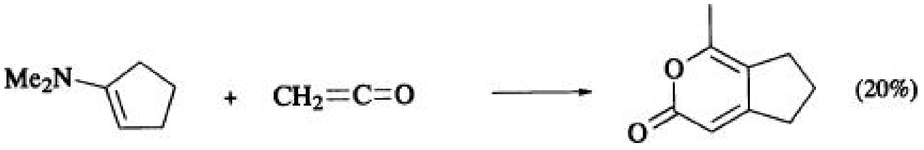
(34)

Products other than the normal [2 + 2] adduct are common in reactions of enamines. Methylvinylketene gives mostly [4 + 2] products in methylene chloride at room temperature, with increasing amounts of cyclobutanone when the reaction is run in hexane at 70° (Eq. 35). (97)



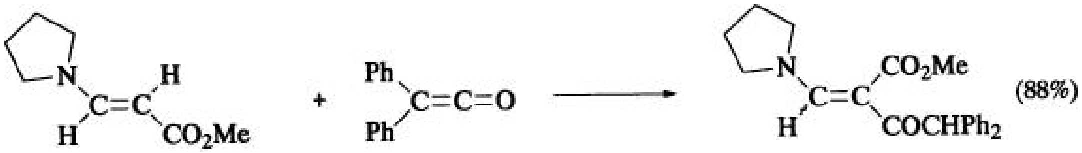
(35)

Two molecules of the ketene often react with one of an enamine with elimination of amine to give a pyrone (Eq. 36). (98)



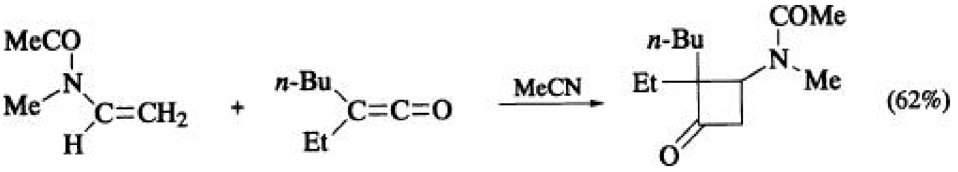
(36)

Acylation of the enamine competes with cycloaddition, and linear products are often obtained (Eq. 37). (99)



(37)

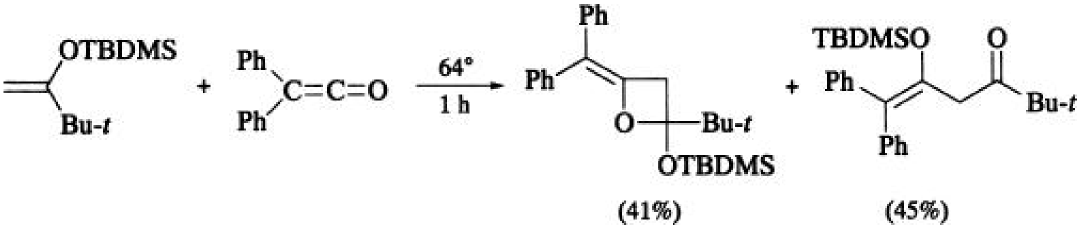
Enamides require higher temperatures to react than enamines, and give stable isolable cyclobutanones in good yield (Eq. 38). (100) Byproducts are not common.

 (38)

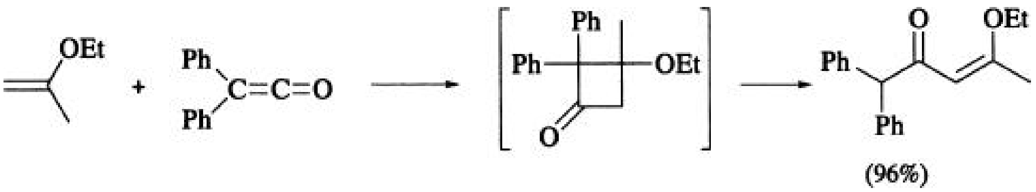
3.1.1.7. Enol Ethers

Olefins substituted with an ether oxygen react much more rapidly than simple alkenes. Even ketene itself, which usually dimerizes faster than it cycloadds to simple alkenes, reacts readily with 1-methoxycyclohexene to give the cyclobutanone in 60% yield. (101) As with simple alkenes, stereochemistry is retained in the cycloadduct, and regiochemistry is consistent with electronic effects. As was noted in the Mechanism section, a small amount of stereochemical “leakage” occurs, even with a relatively simple reactant, propenyl propyl ether. (47) This small loss of stereospecificity does not detract from the general synthetic utility of the reaction. Linear products are also obtained. Ring-opened structures are occasionally seen with 1,1-disubstituted enol ethers, where steric bulk may inhibit ring closure with disubstituted ketenes. In one case, it has been argued that the linear species is not a secondary product arising from rearrangement of the initially formed cyclobutanone, but instead results from rearrangement of a zwitterionic intermediate (Eq. 39). (102)

Although examples of stable 2,2,3,3-tetraalkylcyclobutanones derived from alkenes are common, 2,2,3-trialkyl-3-alkoxycyclobutanones are not often reported,

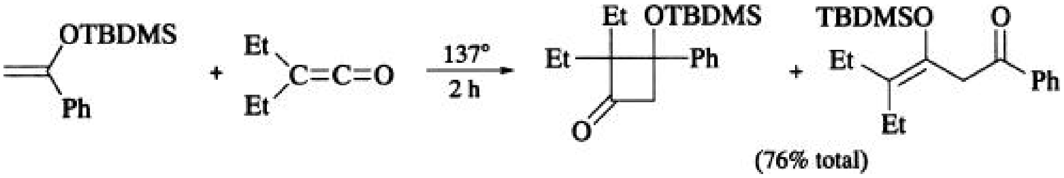
 (39)

perhaps because of the formation of linear products. In the case of 2-ethoxypropene, the cyclobutanone is observed at room temperature, but isomerizes to the linear product during isolation (Eq. 40). (103) Contrary to this generalization,



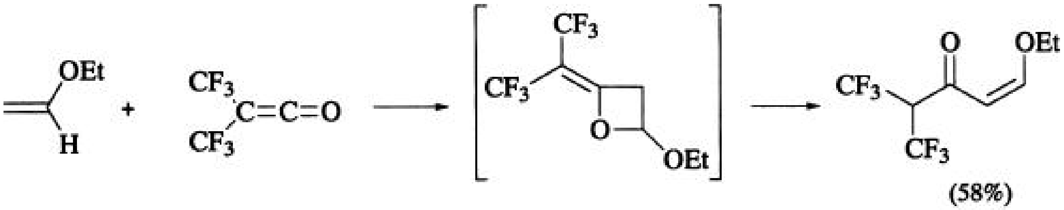
(40)

2,2-dialkyl-3-aryl-3-alkoxycyclobutanones are formed with ease (Eq. 41), (104) as are cyclobutanones with three instead of four substituents in the 2 and 3 positions.



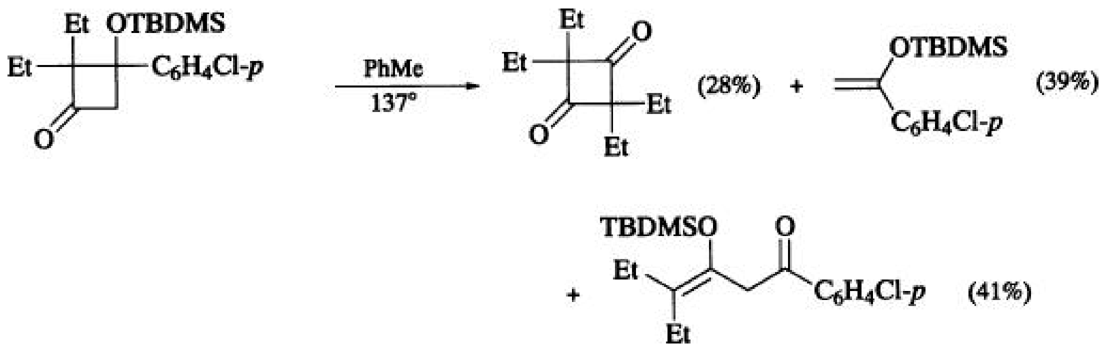
(41)

In a few cases, addition across the carbonyl of the ketene is observed. The oxetane in Eq. 42, which can be isolated, isomerizes to the open-chain isomer. (105)



(42)

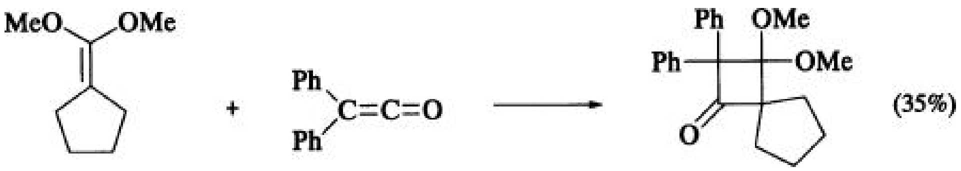
3-Silyloxycyclobutanones revert to ketenes and enol ethers under relatively mild conditions (Eq. 43). (102) Similar behavior is observed for the diphenylmethyleneoxetane in Eq. 39. (102)



(43)

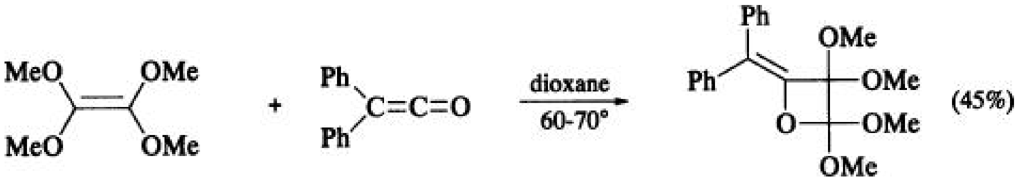
3.1.1.8. Polyoxygenated Olefins

Olefins with two to four ether groups react in the same way as the monoethers, affording oxygenated cyclobutanones (Eq. 44). (105)

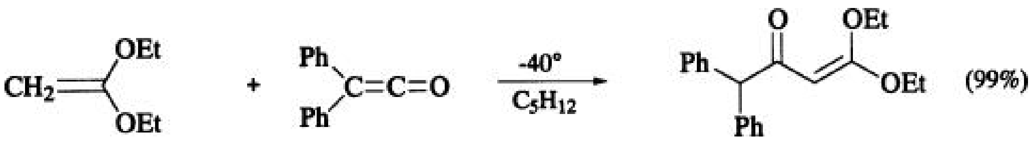


(44)

The chief side reactions are addition across the carbonyl of the ketene (106) and formation of ring-opened products. Tetramethoxyethene reacts with diphenylketene to afford the methylenoxetane, which can be isolated if care is taken to avoid hydrolysis (Eq. 45). (106) Ring-opened ketones are common byproducts with polyalkoxy acetals. Although opening of an initially formed cycloadduct is always a possibility, no cyclobutanone is detected by IR when diphenylketene reacts with 1,1-diethoxyethene at –40° (Eq. 46). (103) Trialkylsilyloxy acetals afford

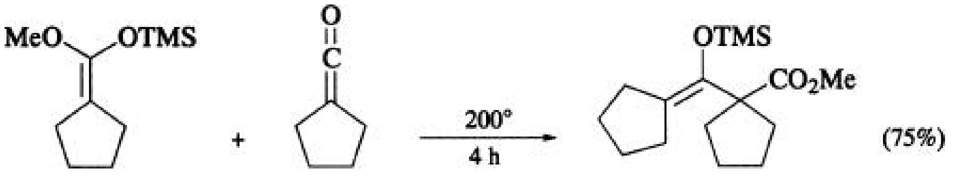


(45)



(46)

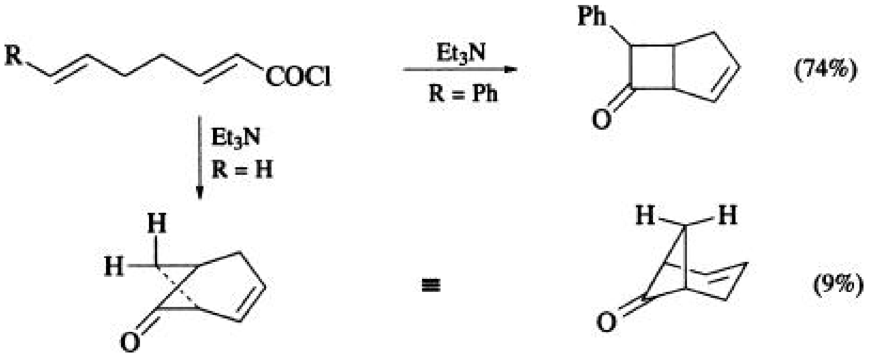
β , γ -unsaturated esters (Eq. 47), (105) even when the α , βisomer is structurally possible. The ring-opened product is easily rationalized by a mechanism involving a zwitterionic intermediate.



(47)

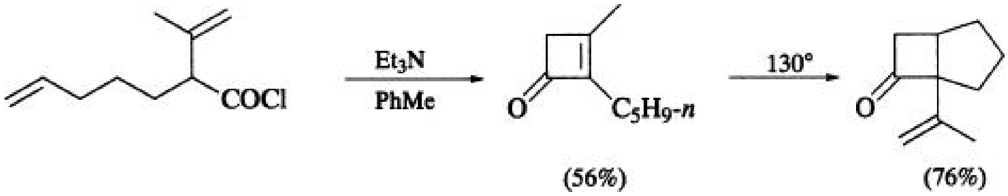
3.1.1.9. *Intramolecular Cycloadditions*

Internal reaction of a ketene with a suitable site of unsaturation on the same molecule occurs readily, and products can be predicted by the same rules used for bimolecular reactions. This reaction has been reviewed. (25) Two modes of internal addition are usually possible, and both products are seen in many instances (Eq. 48). (107)



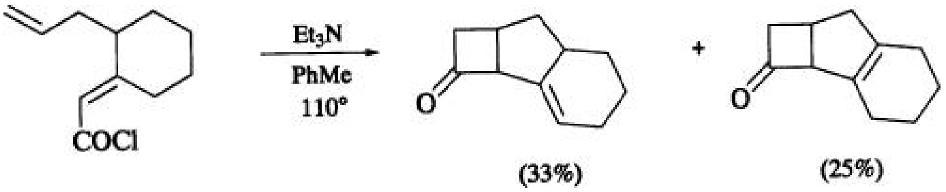
(48)

The chain connecting the ketene and the olefin can be as short as two atoms, but useful results are most often obtained when the connecting link consists of three atoms, yielding 5-membered rings, or four atoms, yielding 6-membered rings. α , β -Unsaturated ketenes form cyclobutenones reversibly when the system contains substitutents on both the ketene and the α carbon, and the β carbon is unsubstituted (Eq. 49). (108)



(49)

In general, when the ketene is generated by dehydrohalogenation of an α , β -unsaturated acid chloride, the proton is removed from the less-substituted γ carbon, regardless of the stereochemistry of the double bond. (109, 110) Exceptions to this rule, however, are not difficult to find (Eq. 50). (110)

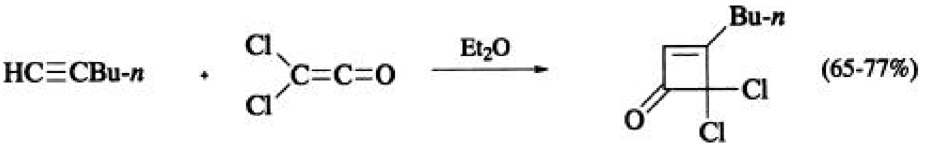


(50)

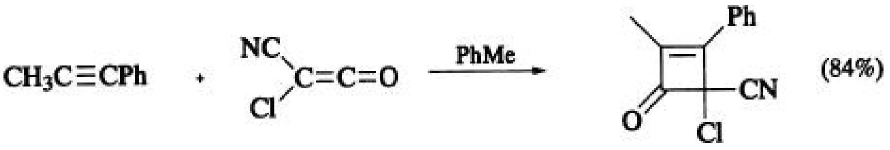
Reactivity patterns follow those of bimolecular reactions of ketenes. Disubstituted ketenes react poorly with unactivated olefins. Good results are obtained with aldoketenes and with ketenes substituted with activating groups such as double bonds, halides, or alkoxy groups.

3.1.1.10. Acetylenes

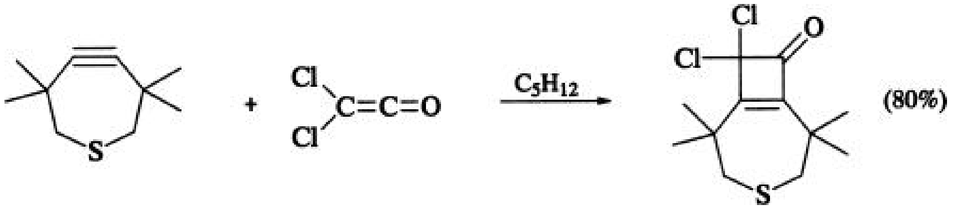
The [2 + 2] cycloaddition of ketenes to acetylenes provides an efficient synthetic route to cyclobutenones. Additions of ketenes to acetylene have not been reported, but reactions of substituted ketenes with both mono- and disubstituted acetylenes proceed in moderate to good yield. Thus 1-hexyne and dichloroketene give a 65–77% yield of 1-butyl-4,4-dichlorocyclobuten-3-one (Eq. 51); (111-113) the regiochemistry demonstrated here is always observed with terminal alkynes. Internal alkynes generally give both possible regioisomers, but reaction of 1-phenyl-1-propyne with chlorocyanoketene in toluene affords the cyclobutenone in 84% yield (Eq. 52). (114) A thiepin alkyne adds to dichloroketene (Eq. 53) to provide a bicyclic product (80%). (60)



(51)

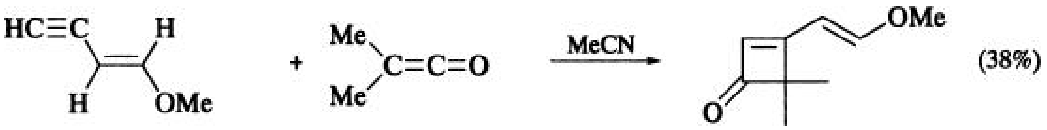


(52)

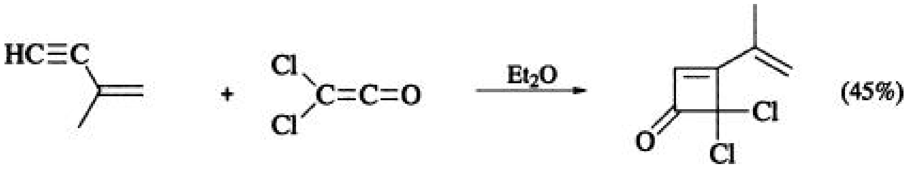


(53)

Alkynes are more reactive toward ketenes than olefins or even enol ethers, and considerable selectivity is seen in the reactions of enynes with ketenes. A cyclobutenone is the only product reported from dimethylketene and 4-methoxy-butenyne (Eq. 54). (115) Similarly, 3-methylbutenyne and dichloroketene give only a cyclobutenone (Eq. 55). (111, 113)

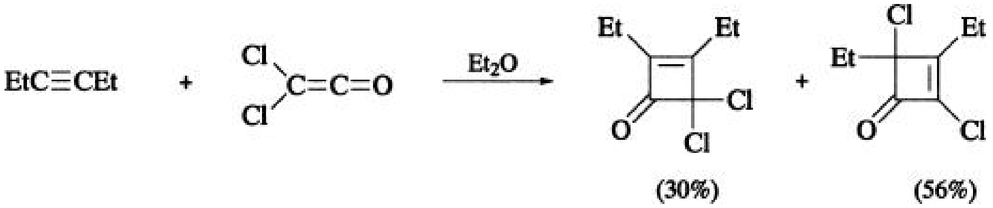


(54)



(55)

It should be noted that rearrangement of the primary dichloroketene-alkyne products to isomeric cyclobutenones can occur as illustrated by the formation of two products in the cycloaddition of dichloroketene to 3-hexyne (Eq. 56). (116) This

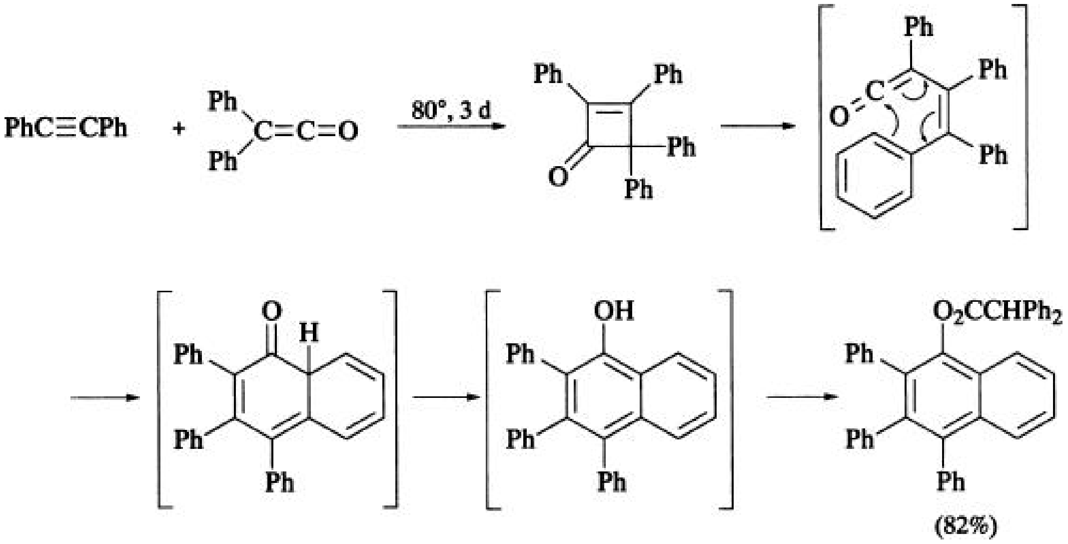


(56)

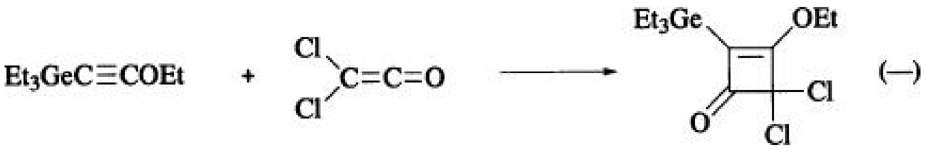
problem occurs when dichloroketene is generated by the trichloroacetyl chloride/Zn-Cu/ $POCl_3$ system; the rearrangement is attributed to the catalytic effect of the byproduct zinc chloride. (116)

Another common rearrangement of an initial ketene–acetylene cycloadduct occurs when the ketene is phenyl-substituted and the reaction is run at elevated temperature. The primary cyclobutenone product undergoes electrocyclic ring opening to provide an intermediate styryl ketene which closes to yield a 1-naphthol derivative. (117, 118) Reaction of the naphthol with excess ketene can lead to 1-naphthyl esters as the ultimate products; the preparation of naphthyl diphenylacetate in 82% yield illustrates the entire process (Eq. 57). (119)

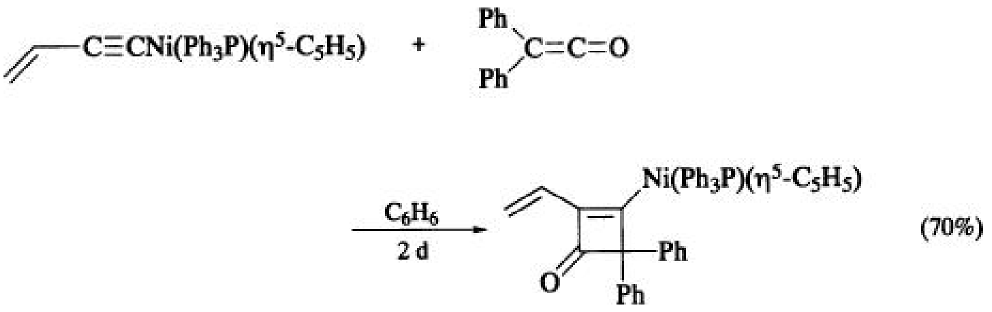
Acetylenes bearing silyl, germyl, arsenyl, phosphoryl, and even transition metal substituents can serve as substrates for [2 + 2] cycloadditions with ketenes. Equations 58 (120, 121) and 59 (122) illustrate such processes. The regiochemistry of cycloadditions involving organometallic acetylenes is generally that seen with simpler alkynes, but silylalkylacetylenes give both possible regioisomers. Thus trimethylsilylpropyne



(57)

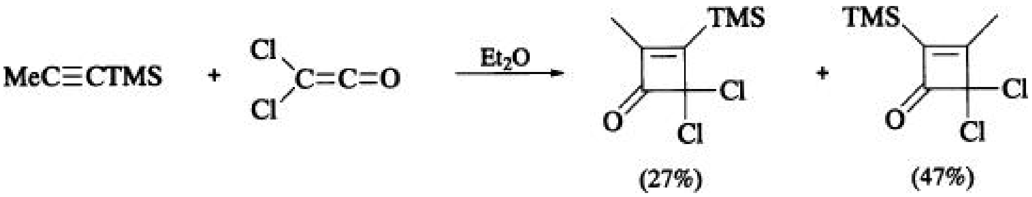


(58)



(59)

and dichloroketene give isomeric cyclobutenones in 27% and 47% yields, respectively (Eq. 60). (120)

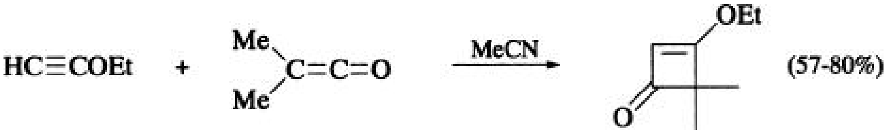


(60)

3.1.1.11. Alkoxyacetylenes

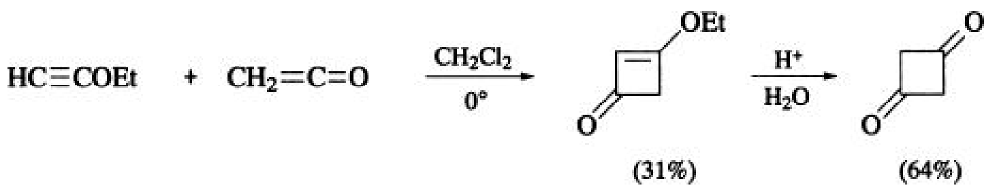
The ketene cycloaddition chemistry of acetylenic ethers departs from that of alkynes through greater reactivity, both in the cycloaddition process and in subsequent rearrangements of the initial cycloadducts, as well as in the occurrence of occasional anomalous reactions.

The regiochemistry of [2 + 2] cycloaddition of ketenes to alkoxyacetylenes is dictated by the electronics of the system and invariably leads to the formation of 1-alkoxycyclobuten-3-ones. The preparation of 1-ethoxy-4,4-dimethylcyclobuten-3-one from dimethylketene and ethoxyacetylene serves to illustrate the process (Eq. 61). (115, 123-128)



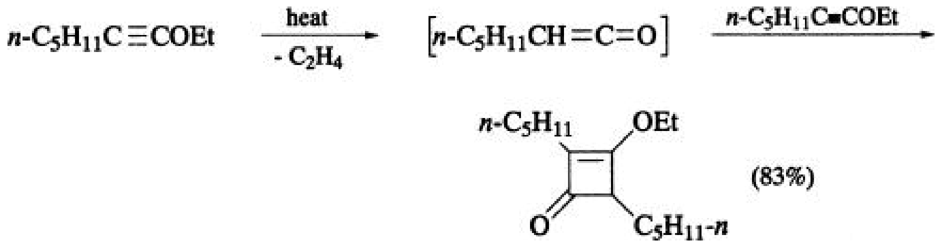
(61)

The 1-alkoxycyclobuten-3-ones have found considerable synthetic utility as precursors to the otherwise inaccessible cyclobutane-1,3-diones (Eq. 62). (126, 127)



(62)

The ketene–alkoxyacetylene system appears insensitive to the method of ketene generation; yields are generally moderate to good and reactions are rapid near room temperature. An early but interesting and synthetically useful method of carrying out these reactions involves simply heating an ethyl 1-alkynyl ether to about 100°. Elimination of ethylene affords an alkylketene which immediately adds to remaining acetylene. Thus 1-ethoxy-1-heptyne gives an 83% yield of cyclobutenone when heated to 120–130° (Eq. 63). (129) In an interesting extension of

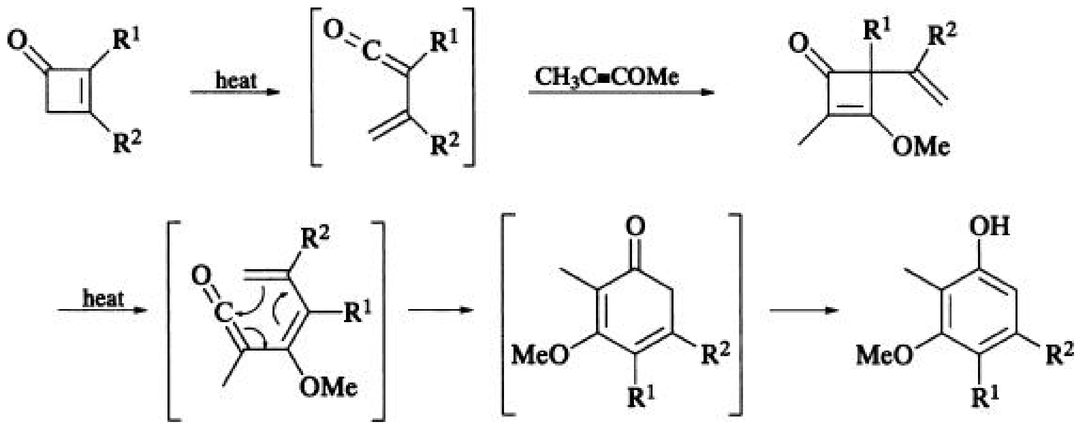


(63)

this method, di-*tert*-butoxyacetylene eliminates isobutylene in benzene at reflux; the resulting *tert*-butoxyketene adds to the acetylene to give a quantitative yield of 1,2,4-tri-*tert*-butoxycyclobuten-3-one (Eq. 64). (130)

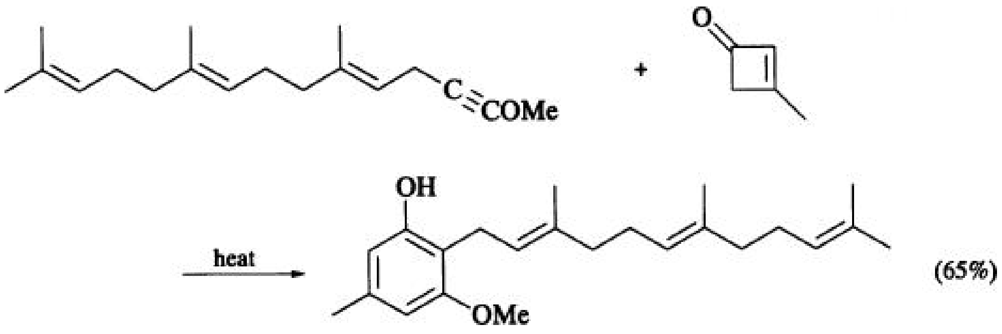
(64)

A useful, high-yielding synthesis of substituted phenols has resulted from the study of the cycloaddition of vinylketenes (generated by thermal rearrangement of cyclobutenones) to acetylenic ethers. The possible [4 + 2] cycloaddition process does not occur, and the initially formed [2 + 2] cycloadduct undergoes a cascade of electrocyclic processes at 80–160° to provide the phenolic product (Eq. 65). (131)



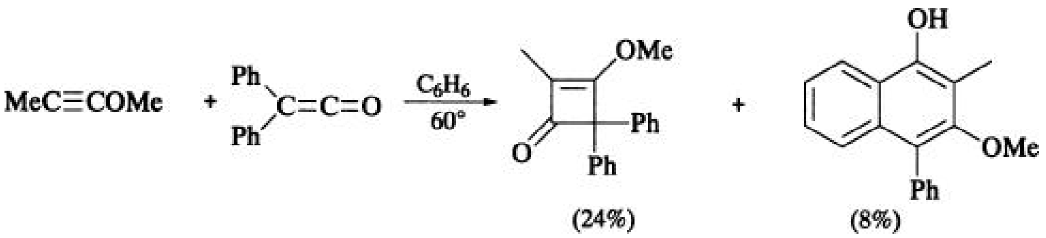
(65)

The formation of isoprenoid phenol from methoxyacetylene and 1-methylcyclobutenone illustrates the use of this sequence in synthesis (Eq. 66). (131)



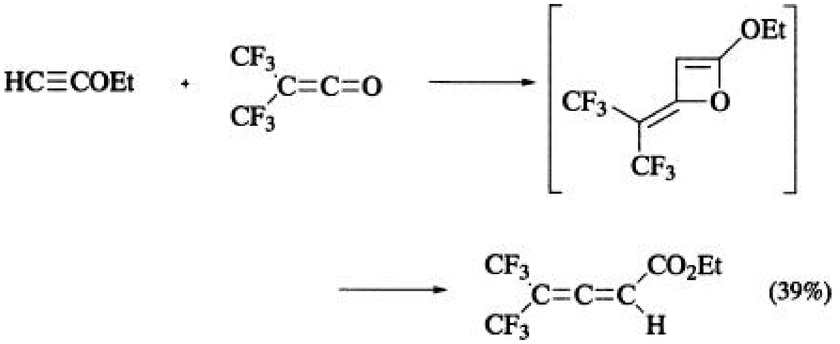
(66)

As was seen with simple acetylenes, reactions of alkoxyalkynes with phenylketenes can lead to substituted 1-naphthols via ring opening and rearrangement of the initially formed cyclobutenone. This process may occur at low temperatures, as in the case of 1-methoxypropyne and diphenylketene in benzene at 60° (Eq. 67): (132)



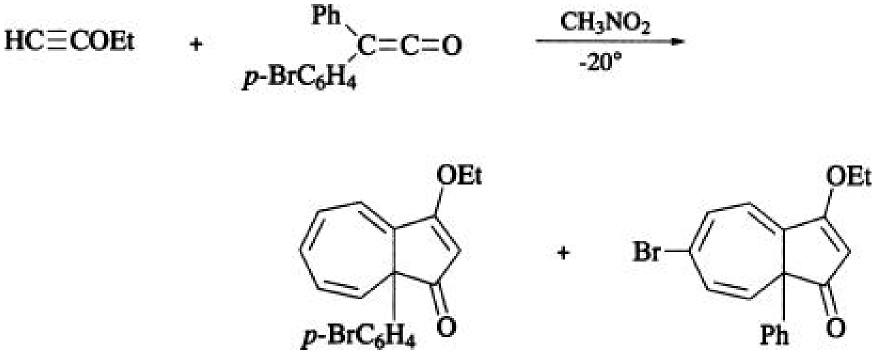
(67)

Two types of anomalous ketene–alkoxyalkyne ether reactions are known. The first is [2 + 2] cycloaddition to the carbonyl group of perfluoroalkylketenes; the resulting oxete can be observed at low temperatures but rearranges to an allene ester upon isolation (Eq. 68). (133)



(68)

The second type of anomalous ketene–alkoxyalkyne ether reaction is that of diarylketenes and ethoxyacetylene in nitromethane solution at subzero temperatures (the expected [2 + 2] adducts and their naphthol rearrangement products are obtained in ether or benzene solution). (126, 132) Thus ethoxyacetylene and phenyl-(*p*-bromophenyl)ketene give a mixture (2.4:1) of isomeric azulenes (Eq. 69). (134)

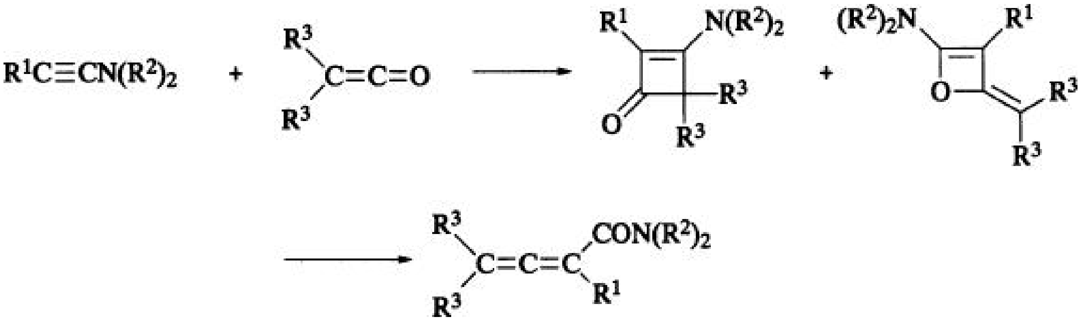


(69)

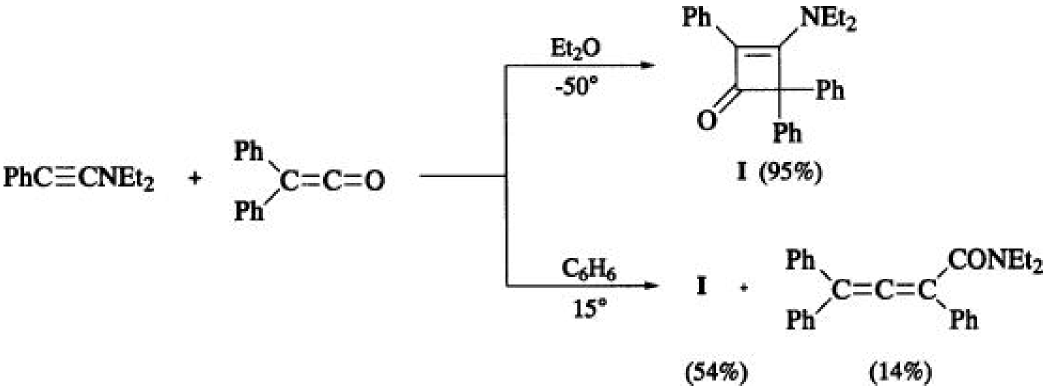
Yields are typically low (ca. 35%); the mechanism of this process has been the subject of considerable research. (132, 134-138)

3.1.1.12. Ynamines

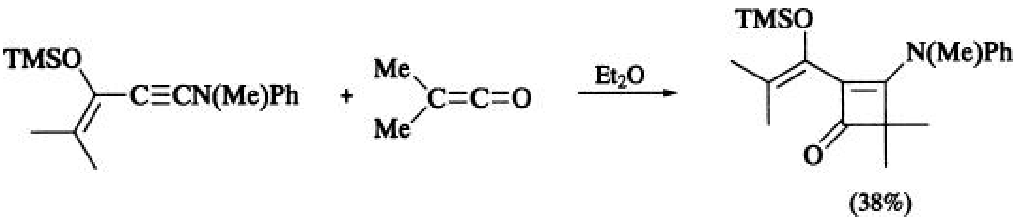
Ketene–ynamine cycloadditions differ from those involving acetylenic ethers and simple acetylenes by their propensity toward [2 + 2] addition to both the olefin and carbonyl moieties of the ketene. The oxete products of reaction with ketene carbonyl groups often undergo rearrangement to allenes in situ (Eq. 70).


(70)

Although a sizable number of ketene cycloadditions with ynamines has been recorded, it is still difficult to predict the outcome of any proposed reaction. Neither steric nor electronic factors consistently appear to control the mode of cycloaddition. The problem is compounded by the fact that yields are often modest; when a low yield of either a cyclobutenone or an oxete (or allene) product is reported, one can only wonder whether the product arising from the alternative regiochemistry was present but not characterized. Furthermore, solvent and temperature effects are not well understood in these reactions. Thus diethylaminophenylacetylene and diphenylketene give a 95% yield of cyclobutenone product when mixed at –50° in diethyl ether; but in benzene at 15°, an allene is obtained in 14% yield along with the cyclobutenone (54%) (Eq. 71). (139, 140)


(71)

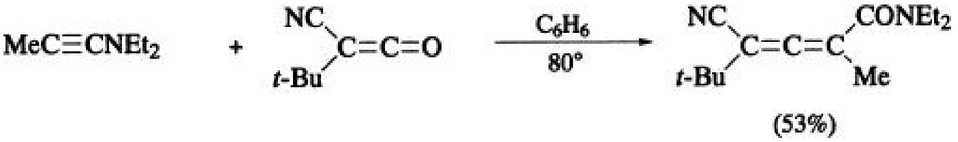
A number of selective cycloadditions involving complex ynamines has nevertheless been successfully carried out. Reaction of the enynamine of Eq. 72 with



(72)

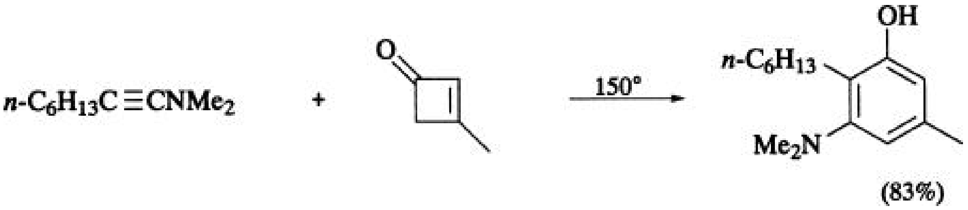
dimethylketene leads to a cyclobutenone in 38% yield; the product of the reaction of ketene with the enol ether moiety was not reported. (141)

That the ketene–ynamine system can be a preparatively useful route to allenic amides is shown by the formation of such a product (53%) by reaction of *tert*-butylcyanoketene with 1-(diethylamino)propyne (Eq. 73). (142)



(73)

The electrocyclic cascade of reactions leading from acetylenic ethers and vinylketenes to phenols has been successfully extended to ynamines. Thermolysis of 3-methylcyclobutenone in the presence of 1-(dimethylamino)octyne affords an 83% yield of aminophenol (Eq. 74). (131) This synthetically valuable reaction illustrates



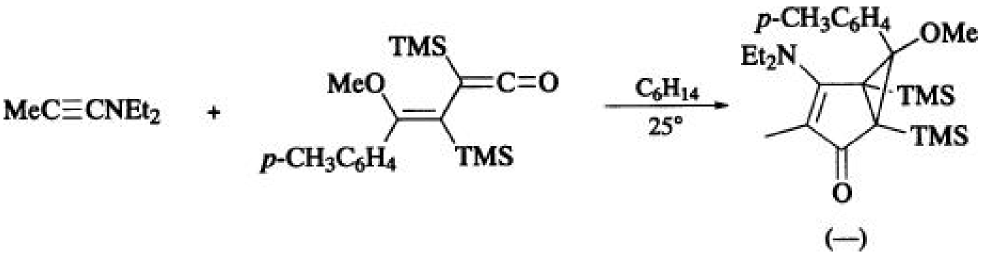
(74)

the potential of ynamine–ketene cycloadditions; however, until more systematic development of the reaction leads to the means to predict, if not control, the regiochemistry of addition, this potential will seldom be realized.

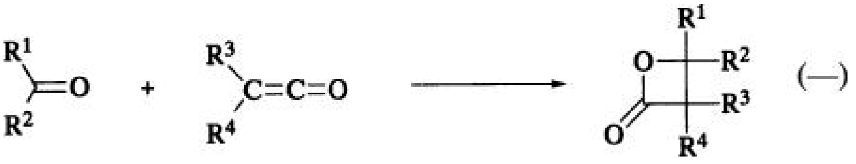
In the reaction of 1-(diethylamino)propyne with silylvinylketenes the initially formed cyclobutenone product rearranges in hexane at 25° to give a bicyclo[3.1.0] product (Eq. 75). (143) This is an alternative outcome of the electrocyclic cascade sequence which has been seen only in heavily silylated systems. (143, 144)

3.1.1.13. Aldehydes and Ketones

The [2 + 2] cycloaddition of ketenes to aldehydes and ketones produces 2-oxetanones (β -lactones) in preparatively useful yields (Eq. 76).

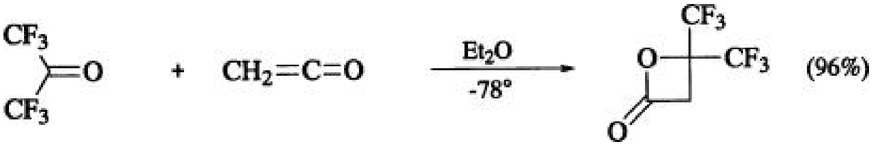


(75)



(76)

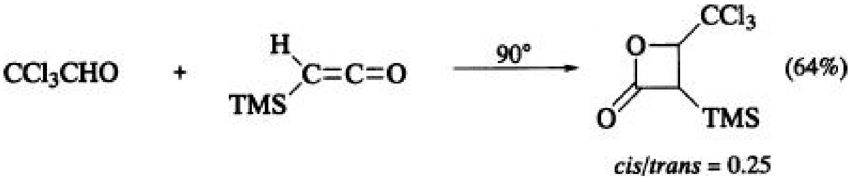
Catalysis is an important factor in most cycloadditions of ketenes to carbonyl compounds. Only systems bearing strongly electronegative substituents, such as carbonyl cyanide or perfluoroketones, react readily with simple ketenes in the absence of catalysts (Eq. 77). (145, 146)



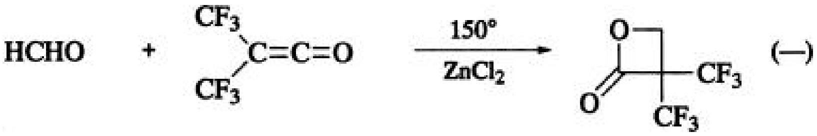
(77)

Most other ketene–carbonyl cycloadditions employ Lewis acids, amines, or amine salts as catalysts. Boron trifluoride etherate, aluminum chloride, and zinc chloride are generally useful; the last is generated in situ when ketenes are formed by dehalogenation of α -halo acid chlorides. Similarly, the trialkylamine and trialkylammonium chloride present when ketenes are produced by dehydrohalogenation of acid chlorides can catalyze the cycloaddition process. Amine catalysis of ketene–aldehyde cycloadditions forms the basis of an important asymmetric induction technique (see discussion below).

Solvents useful in these additions include ethers, halocarbons, and hydrocarbons. Most cycloadditions are carried out at subambient temperatures, but unreactive systems such as trimethylsilylketene and chloral (Eq. 78) (147) or perfluorodimethylketene with formaldehyde (Eq. 79) (148) require heating. In general, low



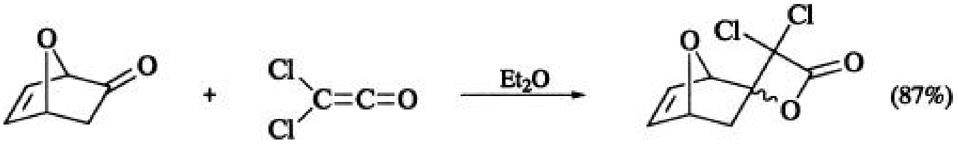
(78)



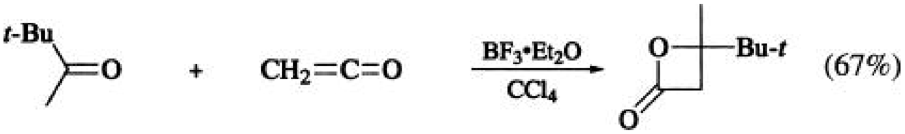
(79)

reaction temperatures are preferred because excess heat can bring about decarboxylation of 2-oxetanones to give olefinic products (see below).

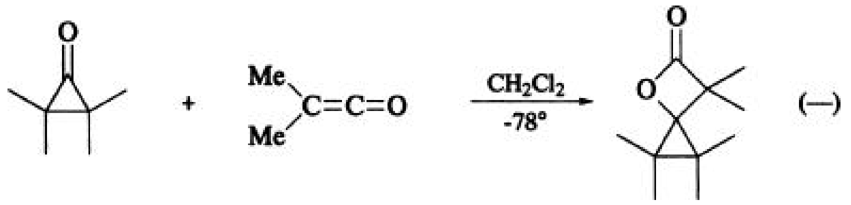
A wide variety of ketene structural types is amenable to this type of cyclo-addition. Ketene itself, alkylketenes, haloketenes, and silyl- or germylketenes have been successfully employed. (147, 149-151) In general, aryl- and diarylketenes are rather unreactive with most aldehydes and ketones, but give good yields of cycloadducts with quinones. (152-154) The cycloaddition process tolerates a wide range of carbonyl substituents, but β-lactone formation from very hindered ketones has not been reported. The preparation of the oxetanones in Eqs. 80, (155) 81, (156) 82, (157) 83, (158) 84, (159, 160) 85, (161) and 86 (162) illustrates the range of reactions possible. The preference



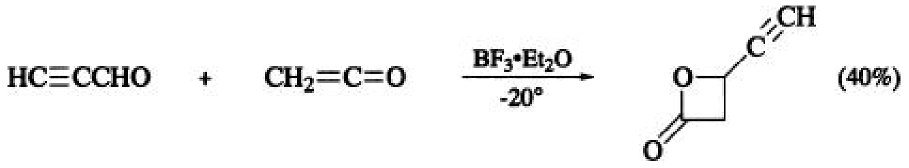
(80)



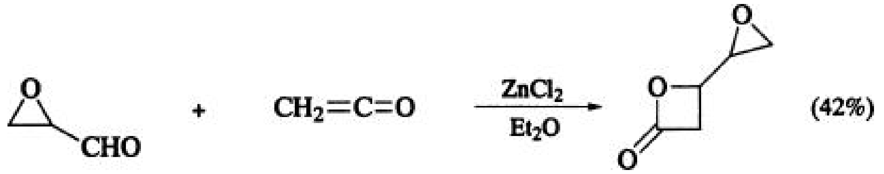
(81)



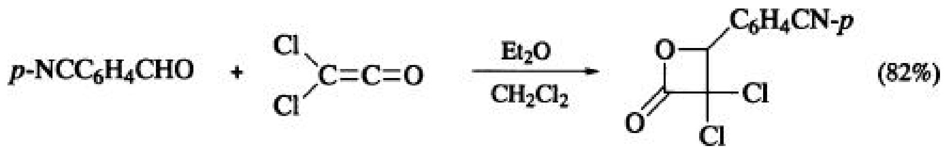
(82)



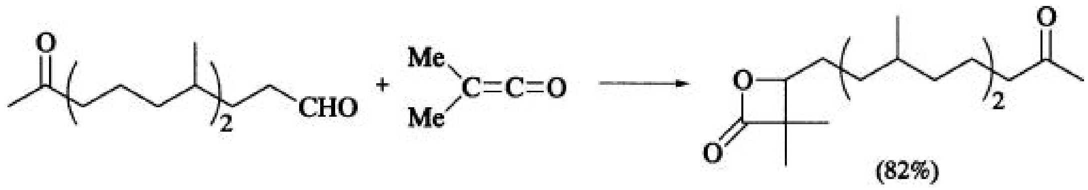
(83)



(84)



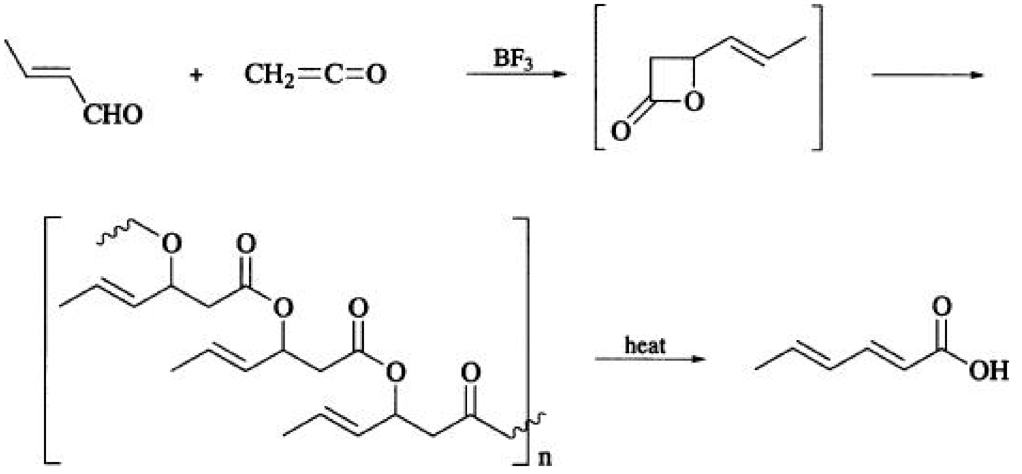
(85)



(86)

for the aldehyde over ketone, alkyne, and olefin functionality (Eqs. 83, 86, and 80) is particularly noteworthy.

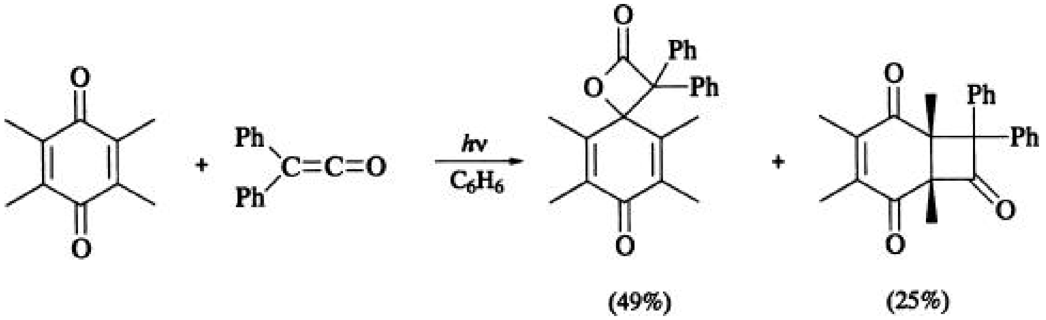
An industrially important application of the ketene–aldehyde cycloaddition is the preparation of sorbic acid from ketene and crotonaldehyde (Eq. 87). This process



(87)

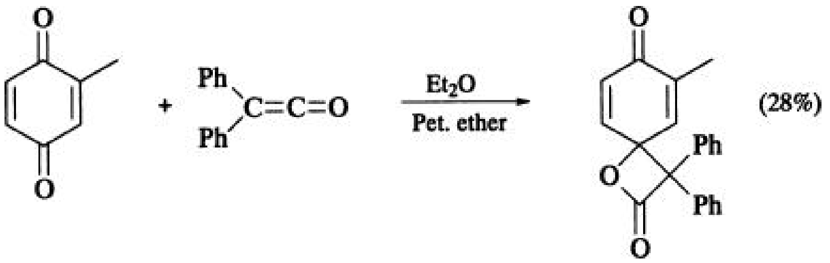
is usually carried out in the presence of boron trifluoride or other Lewis acid catalysts under conditions in which the presumed β -lactone cycloadduct polymerizes to a low molecular weight polyester; formation of the latter is promoted by the presence of transition metal salts of fatty acids. The polyester is thermally degraded to sorbic acid. (163, 164)

Cycloadditions of ketenes to quinones are generally carried out in hydrocarbon solvents at subambient temperature in the absence of catalysts. These reactions display considerable selectivity. Formation of β -lactones generally prevails over cycloaddition to the olefinic unsaturation; one rare example of poor selectivity is the reaction of durenequinone and diphenylketene, from which both lactone and cyclobutanone are obtained (Eq. 88). (153)



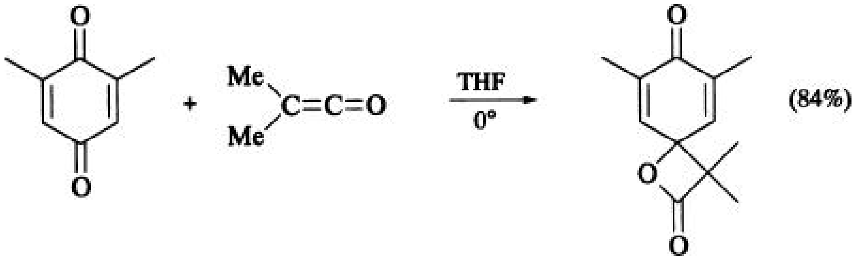
(88)

Ketene–benzoquinone cycloadditions are quite subject to steric influences. The less-hindered lactone is the sole product reported from toluquinone and diphenylketene (Eq. 89), (152) and 2,6-dimethylquinone and dimethylketene likewise



(89)

afford a single lactone (Eq. 90). (165) No examples of double cycloaddition to benzoquinones have been reported.

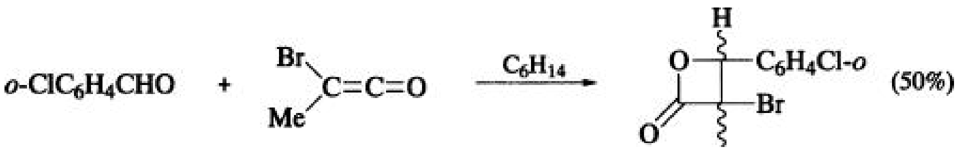


(90)

3.1.1.14. Stereochemistry of Carbonyl Cycloadditions

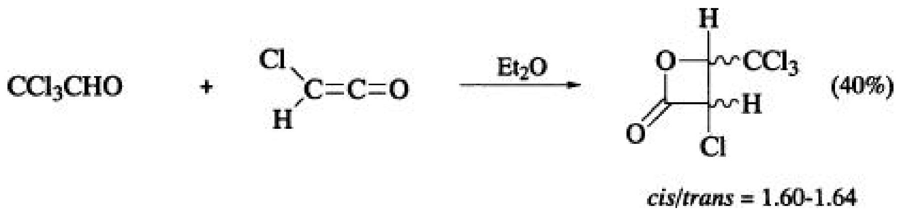
The question of stereochemistry arises in the reactions of aldehydes or unsymmetrical ketones with monosubstituted or unsymmetrically disubstituted ketenes. Unfortunately, many such cycloadditions were described in the older literature wherein the stereochemistry of the product was not determined. There do not appear to be any published examples in which the stereochemistry of a ketone–ketene cycloaddition has been proven.

In aldehyde cycloadditions to monosubstituted and unsymmetrically disubstituted ketenes, mixtures of *cis* and *trans* isomers are generally obtained. In many cases the ratio of *cis* to *trans* products is close to 1; the range is typically from 0.25 to 1.6. Thus *o*-chlorobenzaldehyde and bromomethylketene give a 1:1 mixture of *cis* and *trans* lactones in 50% yield (Eq. 91), (151) and chloral reacts with



(91)

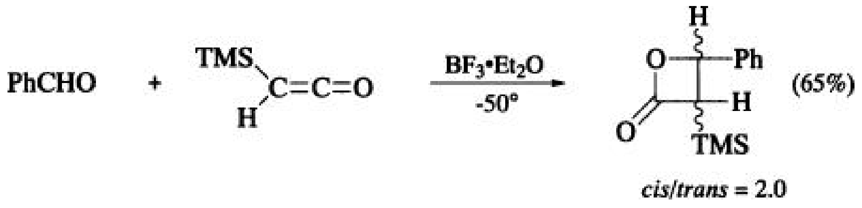
chloroketene to afford a 40% yield of products wherein the *cis/trans* ratio is 1.6 (Eq. 92). (150) Isopropylketene and chloral give a *cis/trans* ratio of 0.9 for the oxetanone



(92)

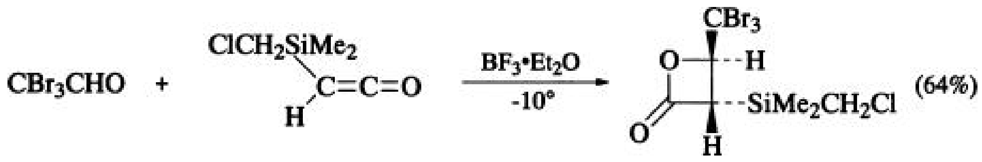
products. (166) In the reaction of monohalo and haloalkylketenes with aldehydes, the *cis* products are formed in slightly greater amounts. (150, 151, 166)

The most extensive set of stereochemical data relating to ketene–aldehyde cycloadditions deals with silyl- and germylketenes. (147, 167) Trialkylsilylketenes add to simple aldehydes in the presence of boron trifluoride etherate to give mixtures in which the *cis* stereochemistry predominates. For example, benzaldehyde and trimethylsilylketene give lactones with a *cis/trans* ratio of 2; with isobutyraldehyde the ratio is 1.5 (Eq. 93). (147)

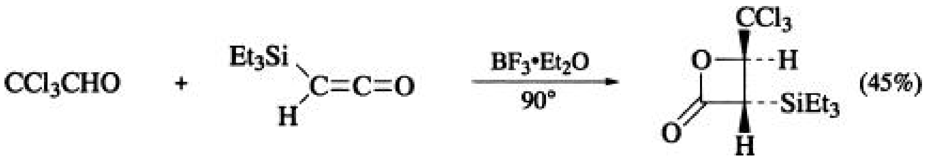


(93)

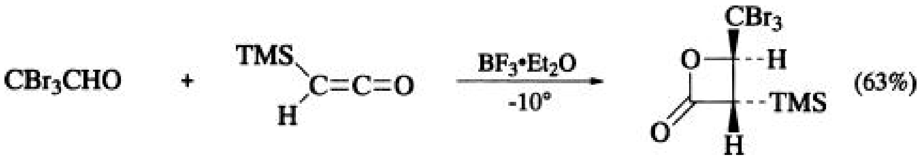
When α -haloaldehydes undergo cycloaddition with silylketenes the stereochemical result contrasts with the poor selectivity, favoring slightly the *cis* product with simple aliphatic aldehydes. In halogenated systems the *trans* isomer predominates and is often the exclusive product. Bromal and chloromethyl-dimethylsilylketene give solely *trans* product (Eq. 94); a similar result is obtained with chloral and triethylsilyketene (Eq. 95). Surprisingly, the stereoselectivity of these cycloadditions is decreased at lower temperatures: bromal and trimethylsilylketene



(94)


(95)

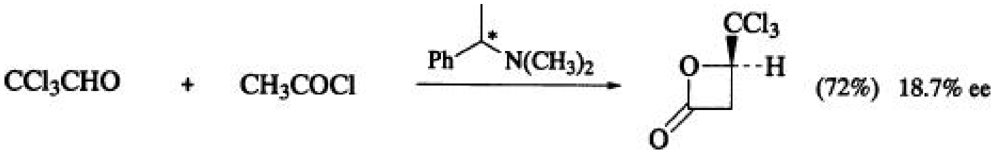
give an 80/20 *trans/cis* mixture at –50°, in contrast to 100% *trans* at –10° (Eq. 96). (147)


(96)

There are obviously many knowledge gaps regarding the stereochemistry of ketene–carbonyl [2 + 2] cycloadditions. The silylketene–haloaldehyde system is the only one reported to give consistently good stereoselectivity. But outside this system there have been few attempts to define systematically the effects of solvent, temperature, catalyst, method of ketene generation, and steric bulk on the stereochemistry of addition; (151) and the stereochemistry of the lactones formed by ketone–ketene cycloaddition is virtually unexplored.

3.1.1.15. Chiral Syntheses

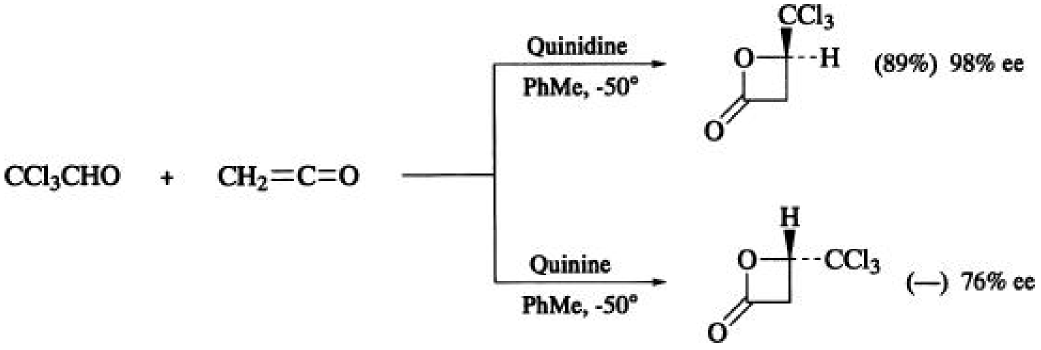
The utility of substituted β -lactones as intermediates in synthesis has led to the development of methods for asymmetric induction in their preparation via ketene cycloadditions. The first successful results in this area came from reactions of halogenated aldehydes and ketones with ketenes generated from aryloxy- or dihaloacetyl chlorides and (–)-brucine or (–)-*N,N*, α -trimethylphenethylamine as dehydrohalogenation reagents. Thus acetyl chloride and chloral, in the presence of (–)-*N,N*, α -trimethylphenethylamine give a 72% yield of (*R*)-(–)- β -trichloromethyl- β -propiolactone of 18.7% optical purity (Eq. 97). (168, 169) Other


(97)

related systems give similar results, and the requirement for a molar equivalent of the chiral base makes the method one of limited synthetic value.

A significant breakthrough in this area came with the announcement that the cycloaddition of ketene with chloral carried out at –50° in the presence of

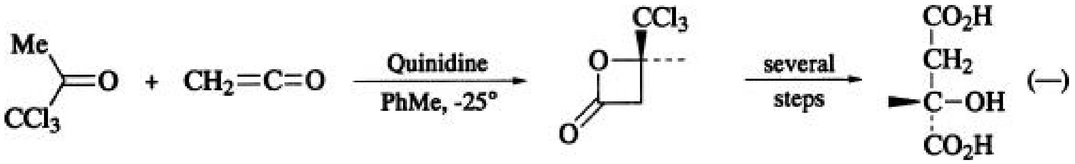
1–2 mol % of quinidine gives an 89% yield of β -lactone having 98% ee of the *R* configuration (Eq. 98). When quinine is used as the catalyst, (*S*)-(+)-lactone is



(98)

obtained with 76% ee; either enantiomer can be recrystallized to optical purity. (170) It should be noted that the original assignment of the *S* configuration to the ketene–chloral adduct obtained with quinidine catalysis was in error; the *R* configuration is in fact obtained with quinidine. (171)

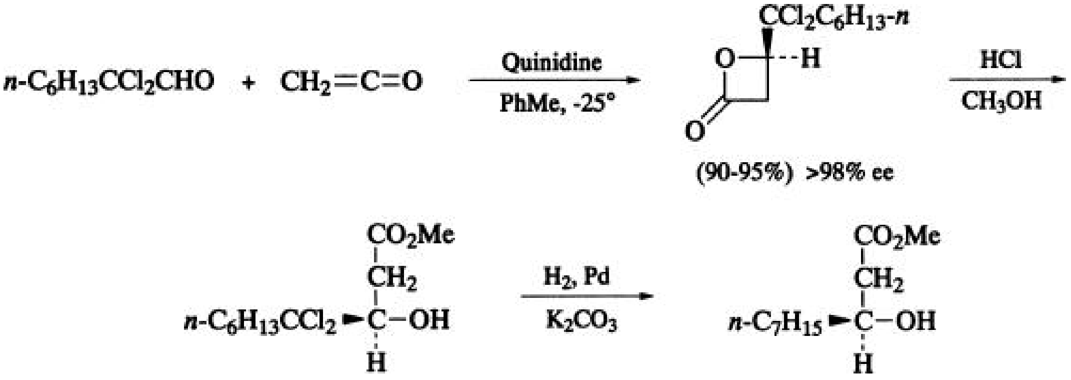
A large number of chiral amine catalysts has been examined, and the cinchona alkaloids are the most effective. A plausible mechanism for the chiral induction, based on formation of an intermediary ketene–amine complex, has been described. (170) The method has been explored in some detail, and excellent results are obtained with both α -halogenated aldehydes and ketones. (171) This method has been applied to the synthesis of, among others, (*R*)- and (*S*)-malic acids, (170) (*R*)- and (*S*)-citramalic acids (Eq. 99), (172) and (*S*)-methyl-3-hydroxyalkanoates (Eq. 100). (173)



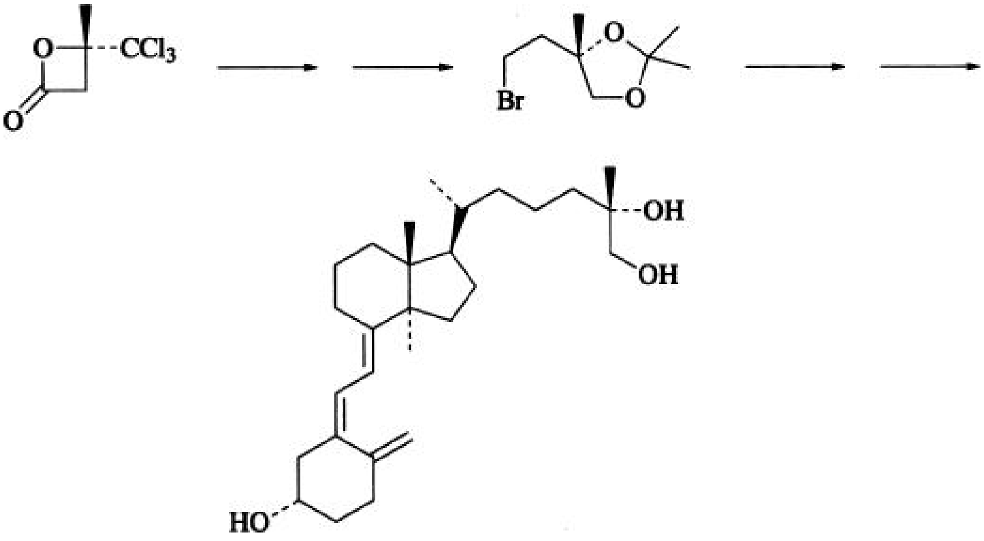
(99)

The acid- and base-catalyzed oxetanone ring-opening reactions used in these sequences proceed with inversion of configuration at the β carbon. This result led to early confusion about the correct absolute configuration of the oxetanones. In another application of asymmetric ketene–aldehyde cycloaddition, the (*S*)-ketene–trichloroacetone adduct was converted into a dioxolane, which has utility in the synthesis of 25,26-dihydroxycholecalciferol (Eq. 101). (174)

Optically active polyesters have also been prepared from the β -lactones obtained from ketenes and haloaldehydes under cinchona alkaloid catalysis. (175, 176)



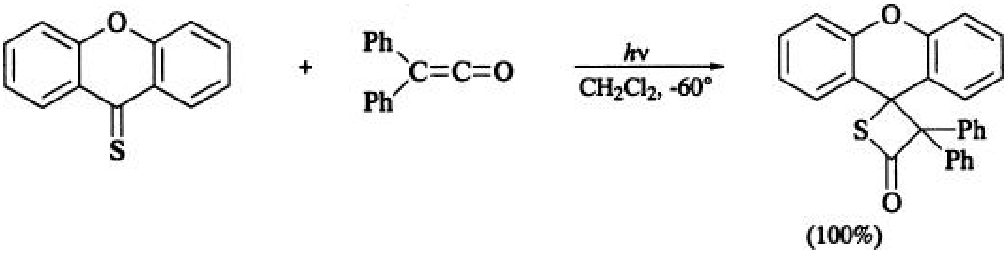
(100)



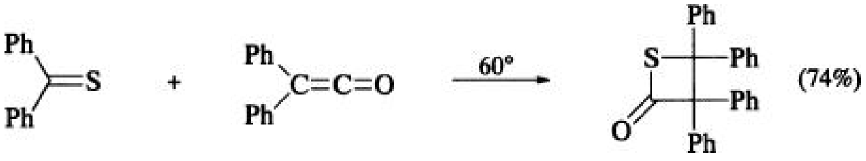
(101)

3.1.1.16. Thiocarbonyl Compounds

Diphenylketene undergoes [2 + 2] cycloaddition to thiones, thioesters, and thioamides to provide thietanone derivatives in good yield. Thioxanthone and diphenylketene give an adduct in quantitative yield upon irradiation, but other thiones such as thiobenzophenone react upon warming to ca. 60° (Eqs. 102 and 103). (177, 178)

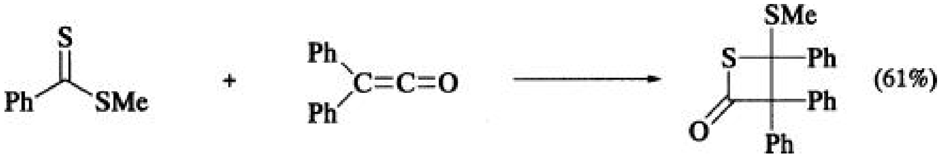


(102)



(103)

Thioester cycloadditions are exemplified by the reaction of methyl dithiobenzoate and diphenylketene (Eq. 104); thioamides react similarly. (177, 179)

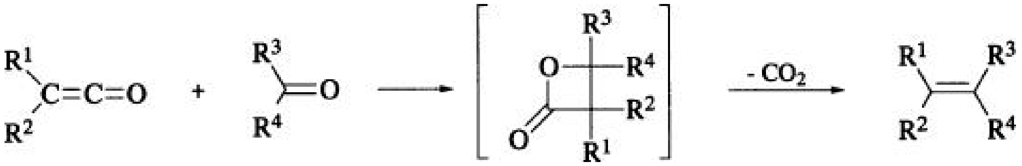


(104)

There appear to be no reported examples of cycloadditions of ketenes other than diphenylketene to thiono compounds.

3.1.1.17. Preparation of Olefins by Reaction of Ketenes with Carbonyl and Thiocarbonyl Compounds

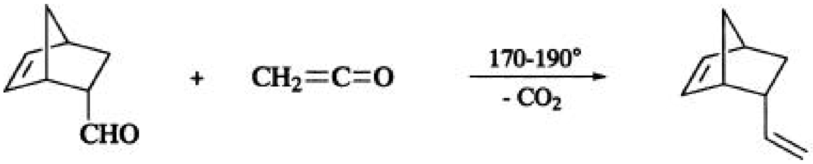
The β -lactones formed by [2 + 2] cycloaddition of ketenes to aldehydes and ketones (and the corresponding thietanones from thiocarbonyl compounds) can be thermally decarboxylated to olefins (Eq. 105).



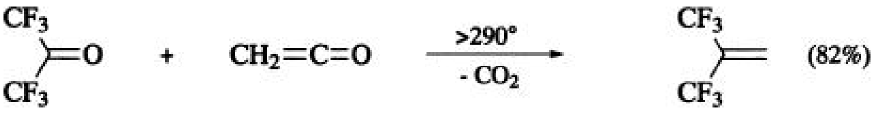
(105)

Since the intermediate lactones need not be isolated and the decarboxylation generally requires a temperature in the range 80–180°, the olefin synthesis in its simplest form consists of heating a ketene and carbonyl compound in an inert solvent until carbon dioxide evolution ceases. Lewis acid catalysts of the type used in the preparation of β -lactones are occasionally employed, but it appears that ketenes commonly react with carbonyl compounds without catalysts at the elevated temperatures necessary for decarboxylation. This olefin synthesis provides a convenient alternative to the Wittig and other similar olefinations; the lack of byproducts and ease of workup argue for wider employment of the ketene-based process.

The simplest examples of aldehydes reacting with ketene have been recorded in the patent literature. Thus it is claimed that vinylnorbornene is produced in 94% yield from the cyclopentadiene–acrolein adduct and ketene at 170–190° (Eq. 106). (180) Gas-phase reaction of hexafluoroacetone with ketene generated in situ from acetic anhydride provides hexafluoroisobutylene (Eq. 107). (181)

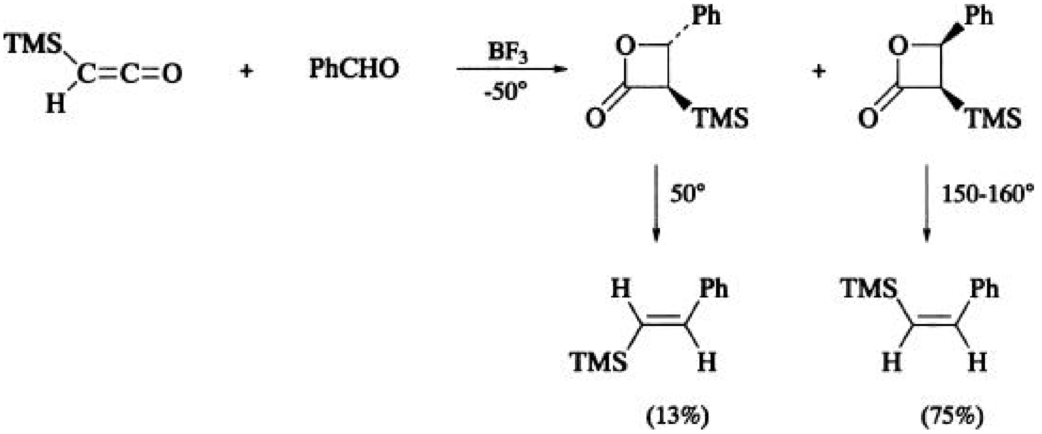


(106)



(107)

The stereochemistry of the olefins produced via β -lactone decarboxylation has not been extensively studied, since most examples involve the use of symmetrical ketenes or carbonyl compounds. However, it is clear that the stereochemistry of the intermediate lactone dictates the final olefin stereochemistry. Thus when benzaldehyde and trimethylsilylketene react in the presence of boron trifluoride at –50°, both *cis* and *trans* lactones are produced. The isolated *trans* lactone decarboxylates at 50° to give the *E* olefin (13% based on aldehyde), whereas the *cis* lactone decarboxylates at 150° to give a 75% yield of the *Z* olefin (Eq. 108). (167)

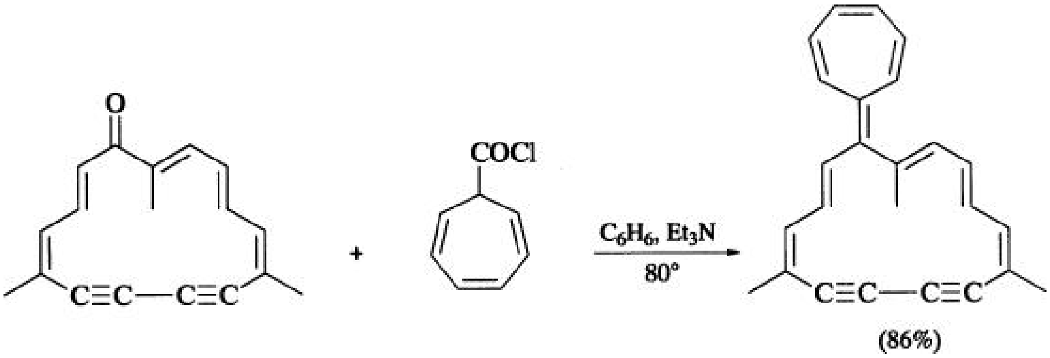


(108)

In a series of reactions of substituted benzaldehydes with various halocyanoketenes, *Z* olefins are formed exclusively. The stereocontrol is attributed to formation of a single β -lactone. Yields range from 8 to 92%, with the higher yields coming from aldehydes bearing electron-donating substituents as in the preparation of the olefin in Eq. 109. (182)

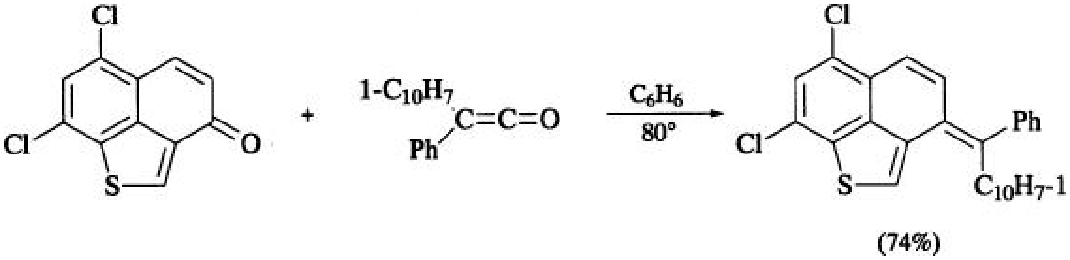
(109)

Carbonyl cycloaddition–elimination to yield olefins is the predominant process even in substrates bearing olefinic and acetylenic functionality, as is seen in the preparation of a complex fulvene in 86% yield (Eq. 110). (183) Furthermore, the



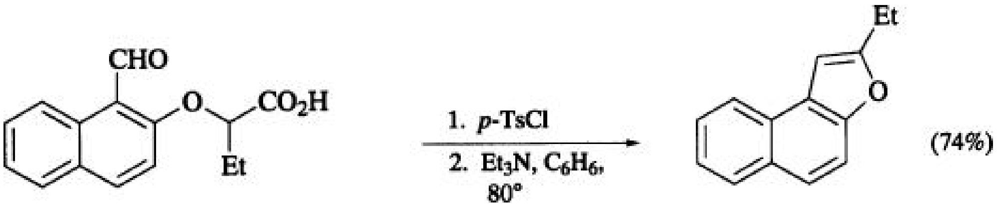
(110)

presence of such potentially nucleophilic sites as divalent sulfur does not lead to side reactions (Eq. 111). (184)



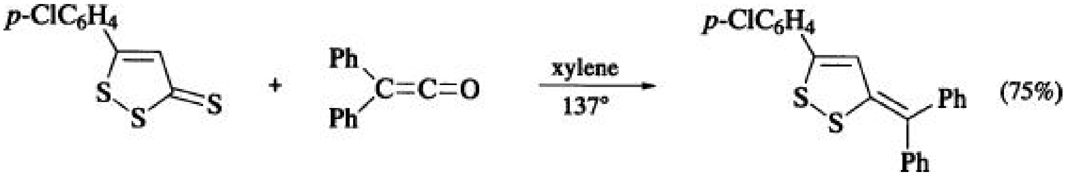
(111)

There is at least one example of selective olefin formation from the aldehyde group of a keto aldehyde and dimethylketene, (162) and a number of intramolecular olefin syntheses proceeding via ketene–carbonyl cycloadditions have been described. The preparation of the naphthofuran of Eq. 112 (185) is typical; we are aware of no extensions of this technology to the synthesis of larger ring systems.



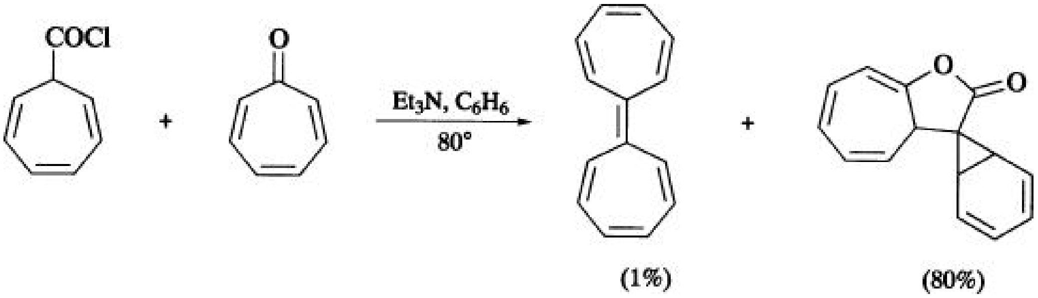
(112)

The elimination of carbonyl sulfide from unisolated intermediate thietanones also provides an olefin synthesis; most recorded examples use thioester substrates (Eq. 113). (186)



(113)

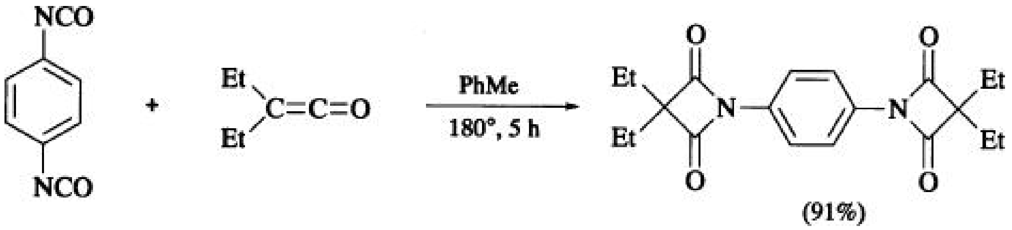
Problematical side reactions occur frequently in olefin syntheses attempted with cycloheptatriene or tropone substrates, as in the addition of the ketene from cycloheptatrienyl 7-carbonyl chloride to cycloheptatrienone; only traces of heptafulvalene are recovered and the major product is a lactone (Eq. 114). (187)



(114)

3.1.1.18. Isocyanates

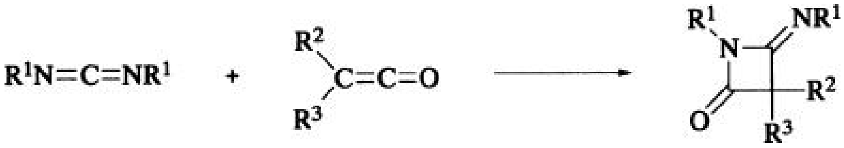
Ketene and alkyl- or aryl-substituted ketenes undergo [2 + 2] cycloaddition to alkyl and aryl isocyanates, usually at elevated temperatures, to give good yields of azetidine-2,4-diones (malonimides). The reaction of *p*-phenylenediisocyanate with diethylketene in toluene at 180° to give a bis(malonimide) is typical (Eq. 115). (188) Sulfonyl isocyanates react similarly, (189, 190) but cycloadditions of haloketenes to isocyanates do not appear to have been reported.



(115)

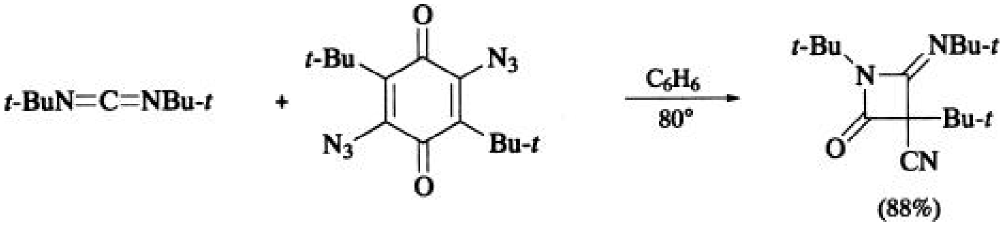
3.1.1.19. Carbodiimides

The reaction of ketenes with carbodiimides yields 4-imino-2-azetidinones (Eq. 116). The cycloadditions take place at am bient or moderately



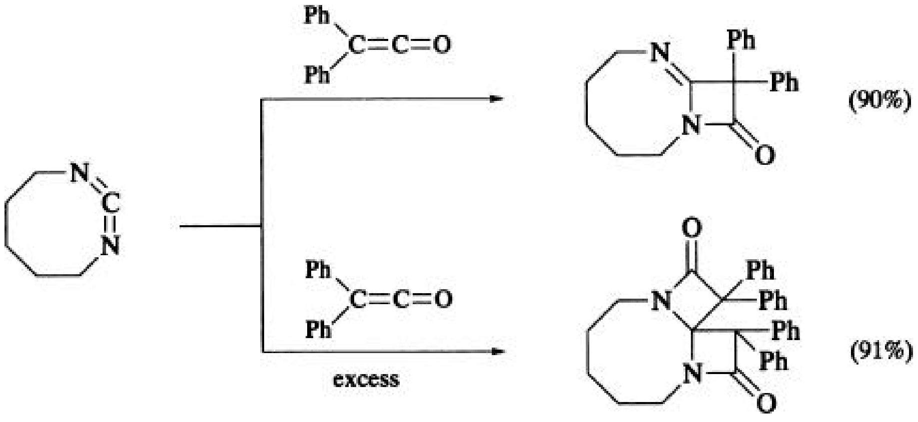
(116)

elevated temperatures in nonpolar solvents; yields are generally good, and the process tolerates a wide variety of ketene substituents. Steric influences are not very important; the preparation of a tri-*tert*-butyllactam from di-*tert*-butylcarbodiimide and *tert*-butylcyanoketene proceeds in 88% yield (Eq. 117). (191)



(117)

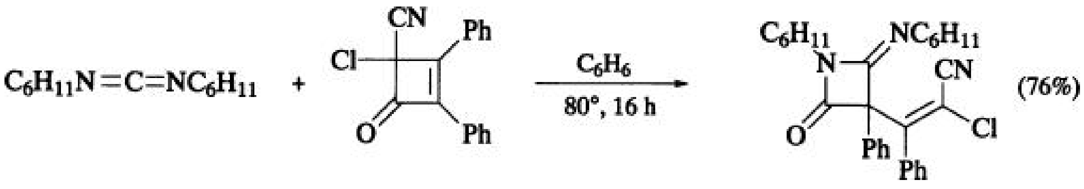
Examples have been reported in which the initial cycloadduct undergoes further reaction with the ketene to provide a spirocyclic product, but this potentially troublesome side reaction can be circumvented by careful avoidance of excess ketene. Thus cyclic pentamethylenecarbodiimide reacts with one equivalent of diphenylketene to give an iminolactam; in the presence of excess ketene, the spirocyclic bis(adduct) is formed in good yield (Eq. 118). (192)



(118)

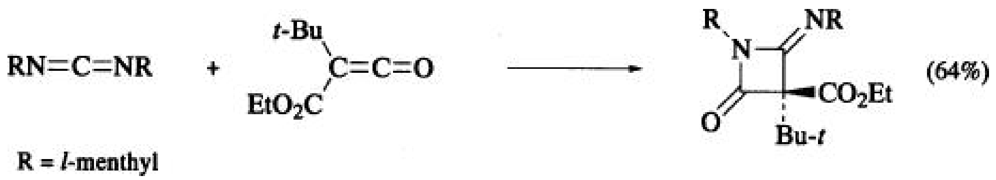
Reaction of dicyclohexylcarbodiimide with the vinylketene formed by ring opening of the cyclobutenone in Eq. 119 gives only the product of [2 + 2] cycloaddition, and overreaction of the ketene with the product is not reported. (114)

A few cycloadditions of ketenes to unsymmetrical carbodiimides have been investigated; poor to moderate yields of single products are reported, but the composition of the entire product mixture remains undetermined. (193) In the reaction of optically active carbodiimides such as dimenthylcarbodiimide with the



(119)

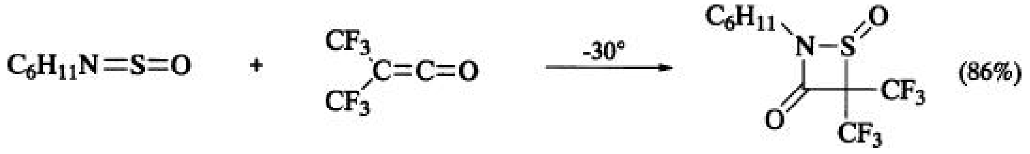
prochiral methylphenylketene, inseparable mixtures of optically active products are obtained. However, when dimenthylcarbodiimide is allowed to react with the ketene as in Eq. 120, an optically active lactam is formed in moderate yield. (194)



(120)

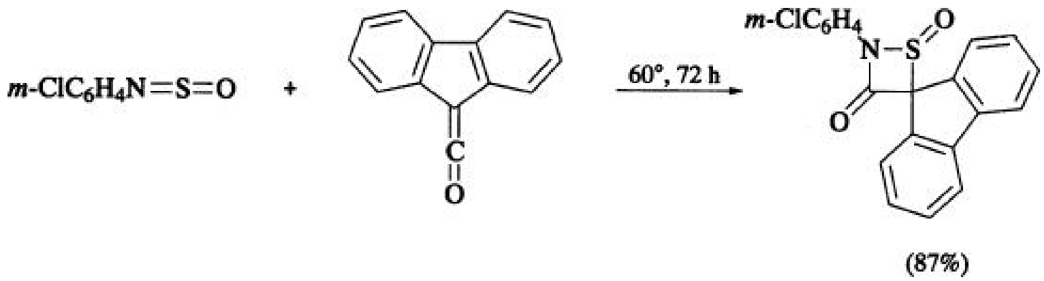
3.1.1.20. N-Sulfinylamines

Ketenes undergo facile [2 + 2] cycloaddition to *N*-sulfinylamines to yield 1,2-thiazetidin-3-one-1-oxides as exemplified by the reaction of cyclohexylsulfinylamine with bis(trifluoromethyl)ketene to give an 86% yield of product (Eq. 121). (195)



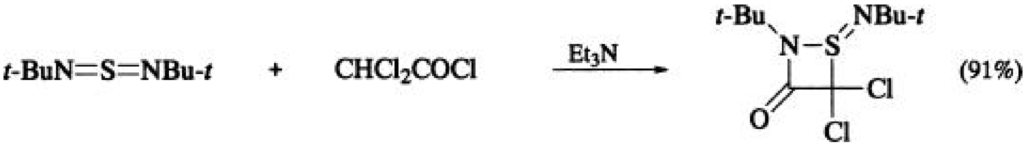
(121)

The process is usually carried out at subambient to ambient temperatures in a wide range of solvents, but fluorenylideneketene reacts with *m*-chlorophenyl-*N*-sulfinylamine only after heating at 60° for 72 hours (Eq. 122). (196) The cycloadducts are generally stable, one exception being the phenylsulfinylamine–ketene adduct, which was prepared and trapped by ring opening with an amine at –78°. (197)



(122)

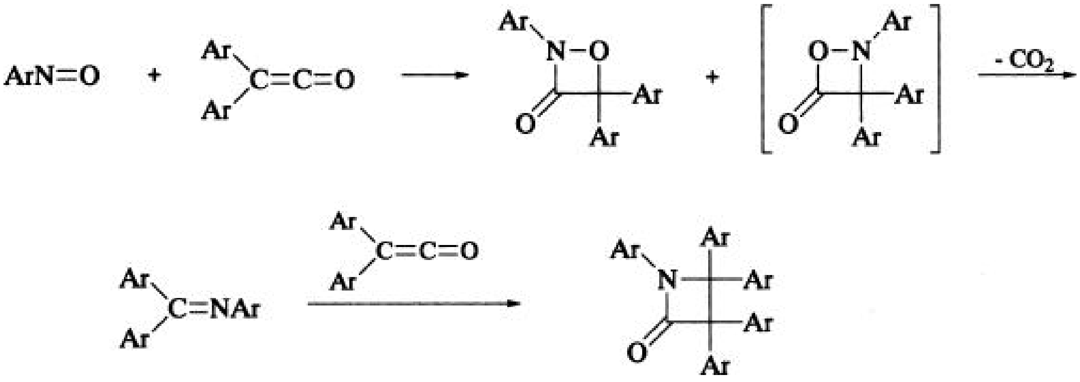
The related dialkylsulfurdiimides also give [2 + 2] reactions with ketenes to form cyclic products (Eq. 123), but diarylsulfurdiimides fail to react with haloketenes. (198)



(123)

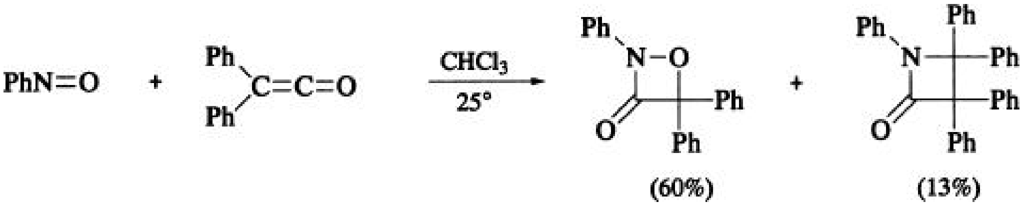
3.1.1.21. Nitroso Compounds

Aryl nitroso compounds react with diarylketenes at ambient or lower temperatures to give product mixtures indicative of poor regioselectivity of cycloaddition. The resulting 1,2-oxazetidin-3-ones are generally stable, but the isomeric 1,2-oxazetidin-4-ones decompose to give carbon dioxide and an imine, which is immediately trapped by additional ketene to give an azetidin-2-one (Eq. 124). (199)



(124)

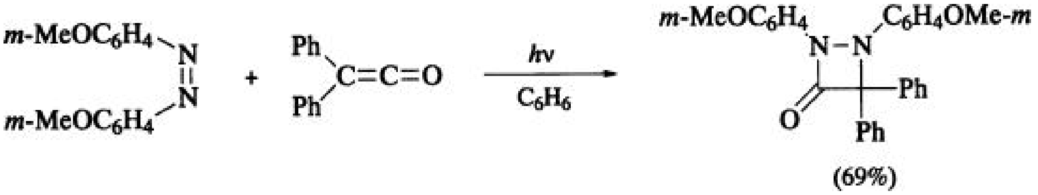
It was at one time thought that the nature of the substitution on the aryl nitroso substrate controlled the regiochemistry and degree of concertedness of the cycloaddition, (200) but more recent results indicate that while oxazetidin-3-ones are the major products, both isomers are generally formed in an apparently nearconcerted process. (199) Thus nitrosobenzene and diphenylketene react in chloroform at 25° to give 60% of 1,2-oxazetidin-3-one and 13% of the β -lactam (Eq. 125). (199) Products from nitroso compounds and alkyl- or haloketenes have not been reported.



(125)

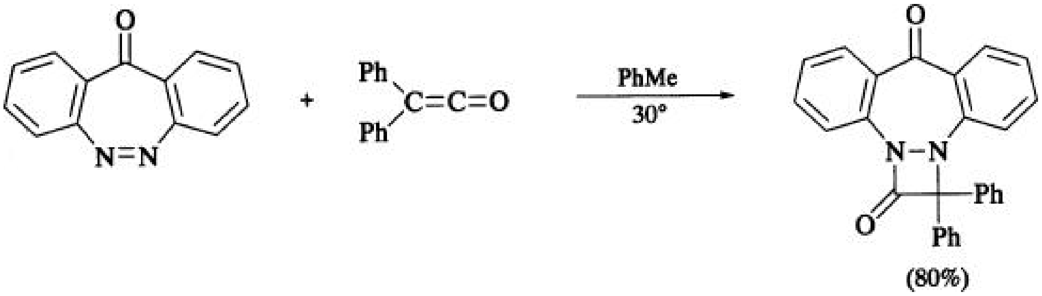
3.1.1.22. Azo Compounds

Ketenes and azo compounds undergo [2 + 2] cycloaddition to yield 1,2-diazetidin-3-ones. Most examples of this process involve symmetrical azobenzenes, which give cycloadducts when irradiated in the presence of ketenes (Eq. 126). (201) It is well established that only the *cis* isomers of azobenzenes



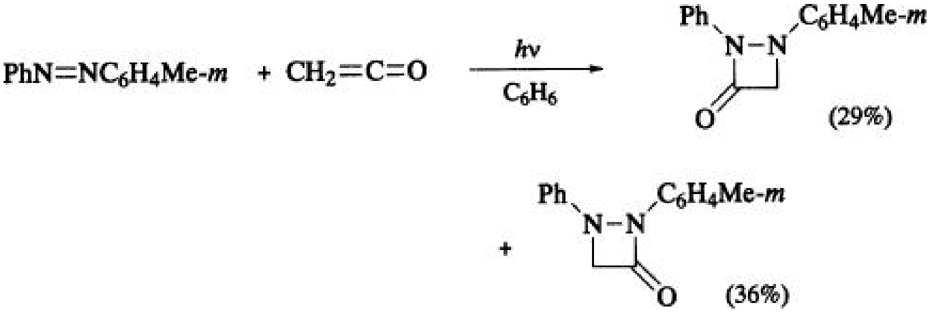
(126)

undergo the ketene cycloaddition process; the reaction of an isolated *cis*-azobenzene with diphenylketene in the absence of irradiation illustrates the point (Eq. 127). (202)



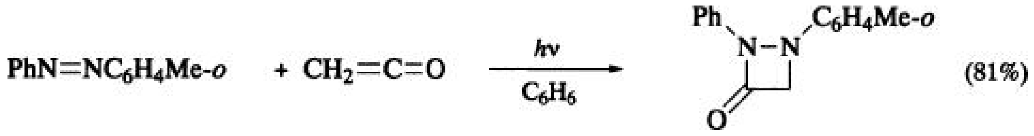
(127)

The use of unsymmetrical azobenzenes in the cycloaddition process generally yields mixtures of regioisomeric products as illustrated by the formation of both isomers from 3-methylazobenzene and ketene (Eq. 128). (203) However, some degree



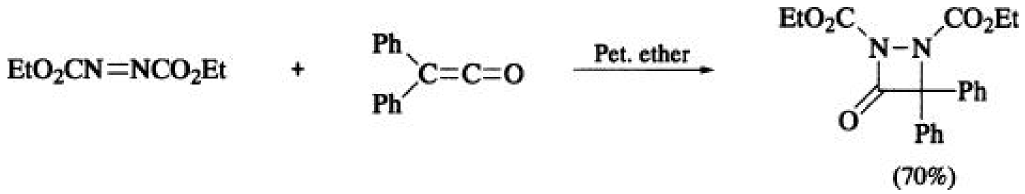
(128)

of steric control of regiochemistry may be possible, since the *o*-methyl analog gives a single diazetidinone with ketene (Eq. 129). (203)



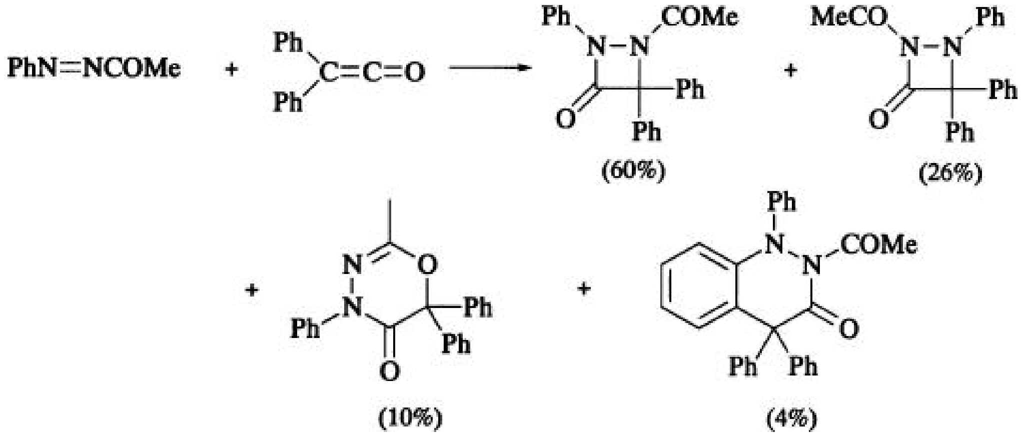
(129)

In contrast to the azobenzenes, azodicarboxylates react with diphenylketene to give cycloadducts without irradiation (Eq. 130). (204) An azoketone also reacts



(130)

with diphenylketene in the dark, but both the orientational selectivity and [2 + 2]/[4 + 2] selectivity are poor, with four products being formed (Eq. 131). (205)

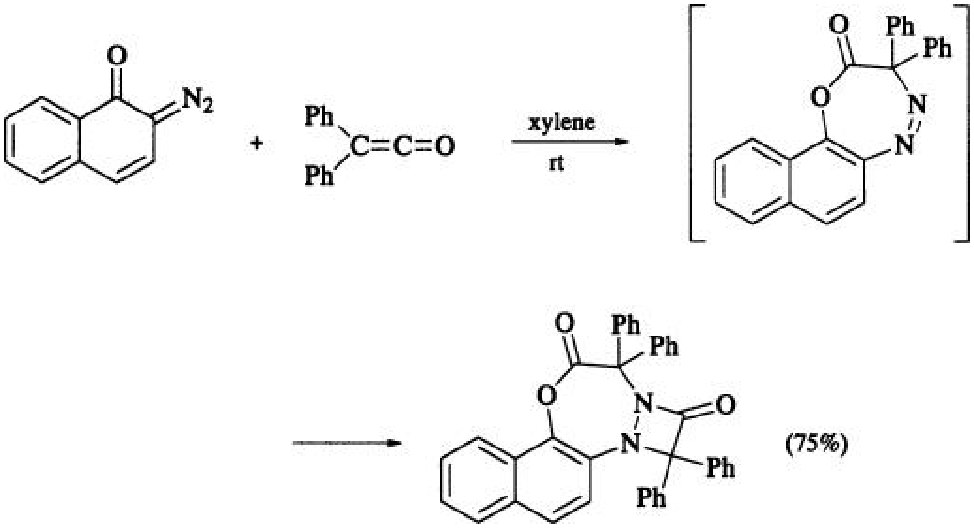


(131)

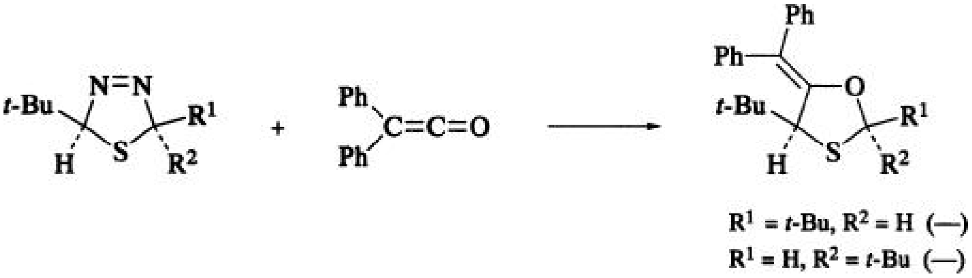
Ketene-azo cycloaddition can occur as a secondary process following other ketene cycloadditions. Thus azoquinones react with diphenylketene to give an unobserved cycloadduct which immediately undergoes a [2 + 2] reaction at the azo linkage to give the final product (Eq. 132). (206)

3.2. [3 + 2] Cycloadditions

Both the carbonyl and the carbon–carbon double bond of ketenes react with 4-electron, 3-center bonds. The retention of stereochemistry by both *cis*- and *trans*-di-*tert*-butylthiocarbonyl ylide in the reaction with diphenylketene is the single case where this criterion for the concertedness of bond formation has been tested (Eq. 133). (207)

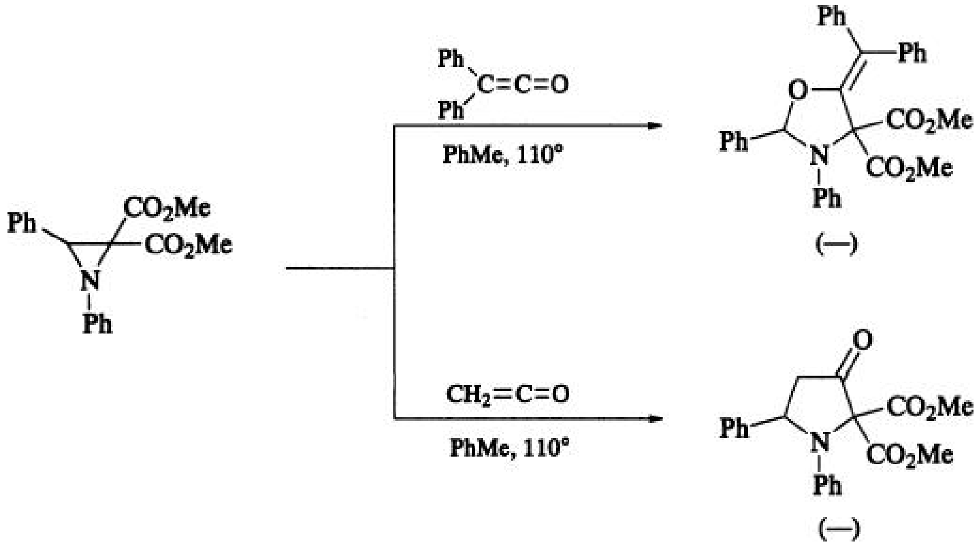


(132)



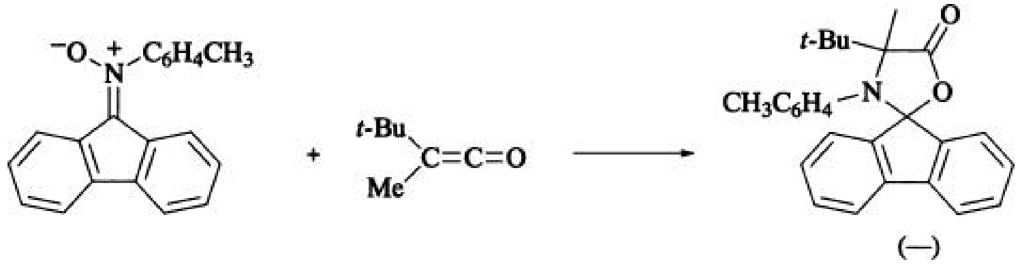
(133)

The azomethine ylide gives different products with ketene and diphenylketene (Eq. 134). (208)



(134)

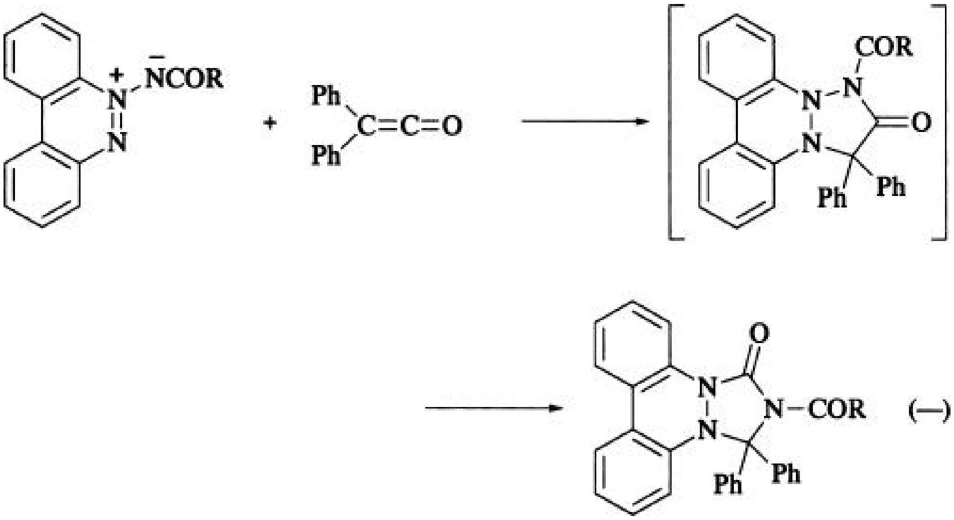
Alkyl- and arylnitrones generally react with ketenes by an ionic pathway to give oxazolidinones (Eq. 135); (209) Table XXVII lists one exception to this rule.



(135)

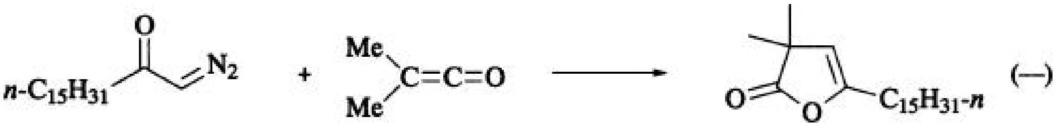
Nitrile oxides react with ketenes, and both isoxazolinone (210, 211) and oxazolinone (212) products have been reported. The structural assignment of an isoxazolinone to the product from the reaction of diphenylketene with *tert*-butylnitrile oxide has been challenged. (212) The support for the isoxazolinone structure was based only on the infrared spectrum, (210) while the oxazolinone structure was based on more extensive analysis. (212)

An azimine reacts with diphenylketene to give a rearranged product (Eq. 136). (213) Trapping experiments suggested the intermediacy of a formal [3 + 2] adduct.



(136)

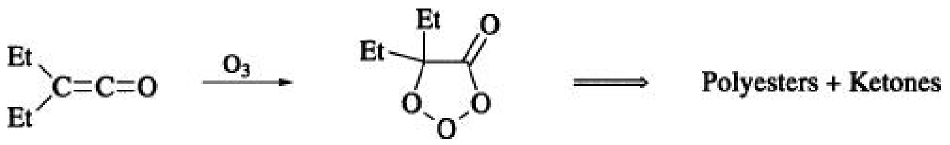
Diazomethane reacts with ketene, (214-217) methylketene, (72) and dimethylketene, (218) as well as with silyl and germanyl ketenes, (219, 220) to give cyclopropanones with no indication of a [3 + 2] process. A rearranged adduct containing two molecules of bis(trifluoromethyl)ketene has been reported. (221) Monoaliphatic and aromatic α -diazoketones give five-membered ring products by an ionic mechanism (Eq. 137). (222, 223)



(137)

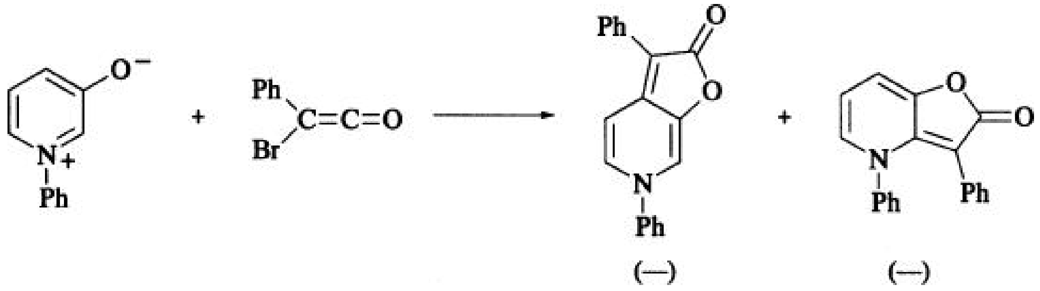
The reaction of *n*-butyl azide with two molecules of diphenylketene is hypothesized to proceed by way of an α -lactam intermediate. (224, 225) The reaction product of two moles of diphenylketene with trimethylsilyl azide is tetraphenyl-succinimide. (226) In both cases, an ionic stepwise mechanism, rather than a cycloaddition, was proposed.

Polyesters and ketones are the isolated products of the reaction of ozone with disubstituted ketenes (Eq. 138). (227-229) The reaction is proposed, by inference from the products, to proceed via a [3 + 2] addition followed by rearrangements.



(138)

Other polar reactants can add to ketenes to give products based on a five-membered ring, as exemplified by the 3-oxidopyridinium betaine in Eq. 139. (230)



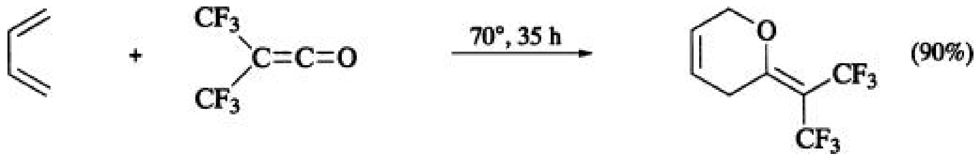
(139)

These processes are probably stepwise ionic reactions leading to cyclic products, rather than true cycloadditions.

3.3. [4 + 2] Cycloaddition of Ketenes

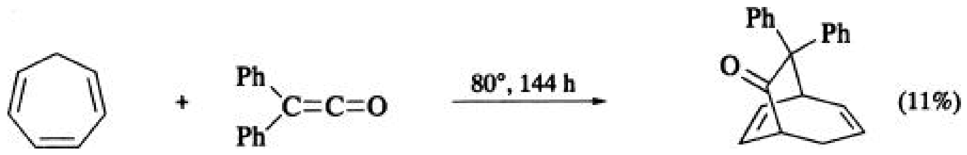
3.3.1.1. Dienes

The [4 + 2] cycloaddition of ketenes to simple dienes and dienic enol ethers to give pyran derivatives has not been developed to the point of general preparative utility. While butadiene reacts with bis(trifluoromethyl)ketene to provide a 90% yield of pyran (Eq. 140), (231, 232) the reaction of cycloheptatriene



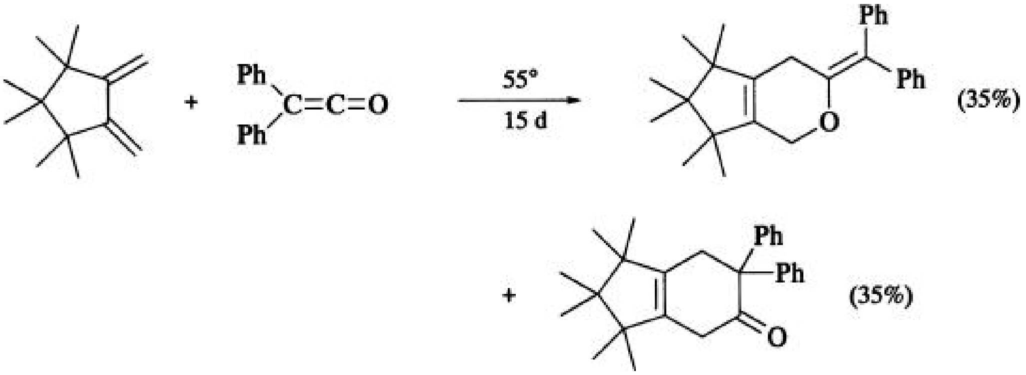
(140)

and diphenylketene to give a bicyclo[3.2.2] product proceeds in only 11% yield (Eq. 141). (233)



(141)

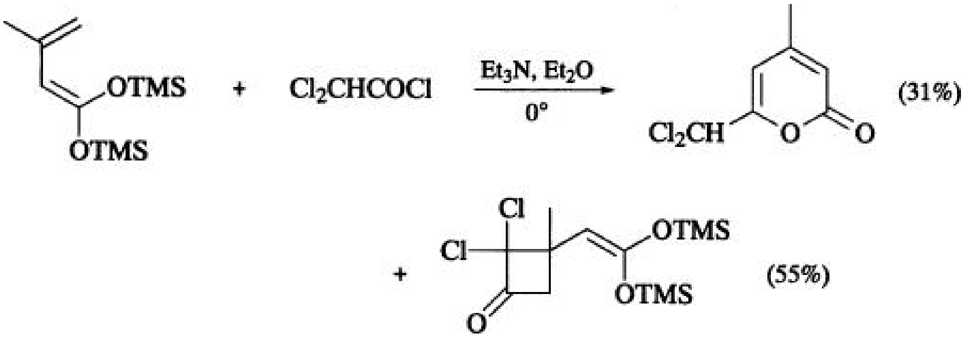
Prediction of product structure from such cycloadditions is complicated by the fact that either the ketene carbonyl group or olefinic linkage can serve as the two-electron component, and both modes of addition are seen in many reactions. Thus 3,3,4,4,5,5-hexamethyl-1,2-bis(methylene)cyclopentaene and diphenylketene give equal amounts of two cycloadducts as shown in Eq. 142. (234)



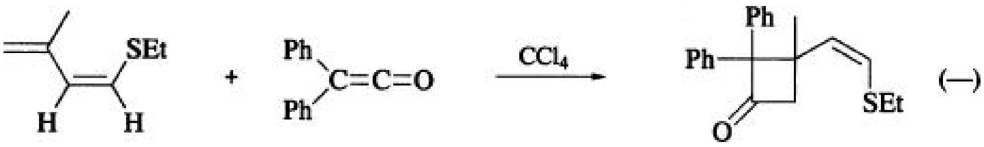
(142)

Competition between [2 + 2] and [4 + 2] cycloaddition often gives rise to mixtures of cyclobutanone and pyran products, as is the case with dichloroketene and the bis(trimethylsilyl)diene of Eq. 143. (235, 236) It is also known that diene geometry can control the outcome of ketene cycloadditions: the (*Z*)-thioether of Eq. 144 and diphenylketene give cyclobutanone, whereas the pyran is formed when the (*E*)-thyioether is employed (Eq. 145). (237)

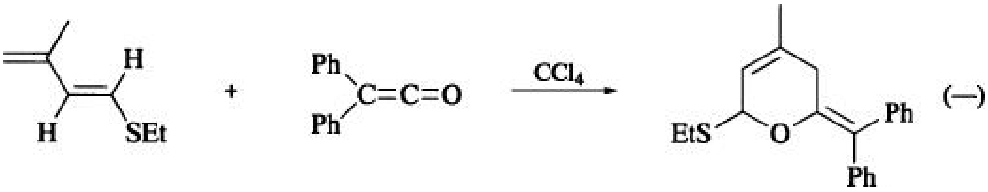
Moderate yields of [4 + 2] cycloadducts are obtained with haloketenes and silyloxydienes. The initial product is hydrolyzed in situ to give the isolable pyranone (Eq. 146). (238)



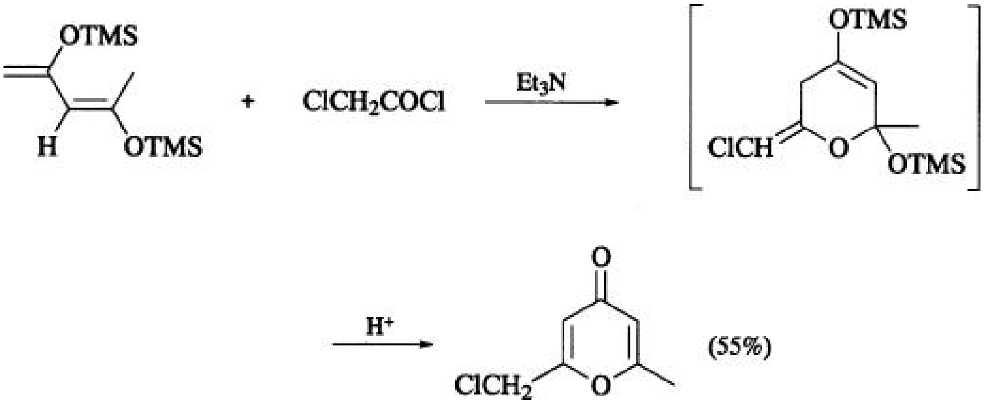
(143)



(144)

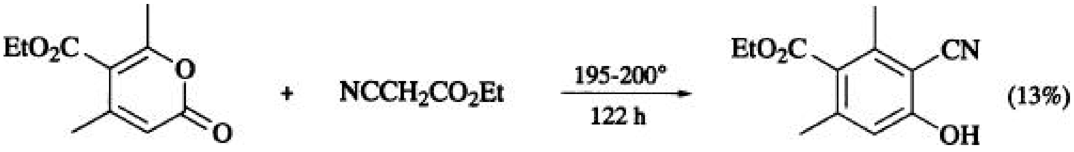


(145)



(146)

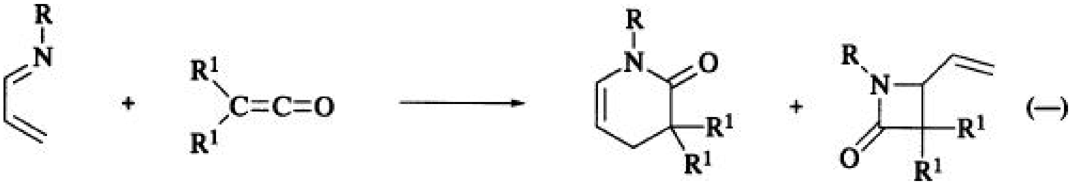
Preparation of phenols by cycloaddition of ketenes to 2-pyranones followed by decarboxylation of the initial bicyclic product generally gives a poor yield (Eq. 147). (239, 240)



(147)

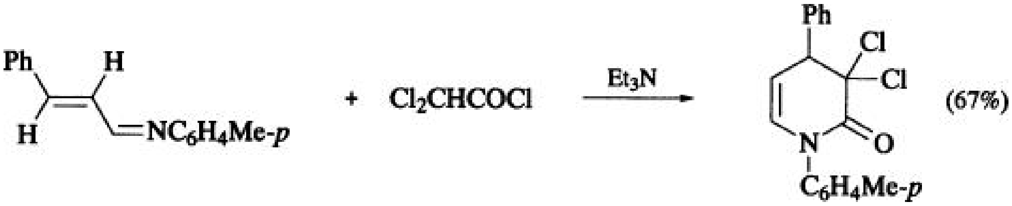
3.3.1.2. Azadienes

Imines of α , β -unsaturated carbonyl compounds (1-azadienes) participate in [4 + 2] cycloaddition reactions with ketenes to produce dihydropyridones. The other possible regiochemistry of addition, leading to 3-ketodihy-dropyridines, is not seen. Although competing [2 + 2] cycloaddition to the imine moiety of azadienes occasionally leads to product mixtures containing β -lactams (Eq. 148), the [4 + 2] process usually proceeds in acceptable yield at ambient or slightly elevated temperatures in the absence of catalysts.



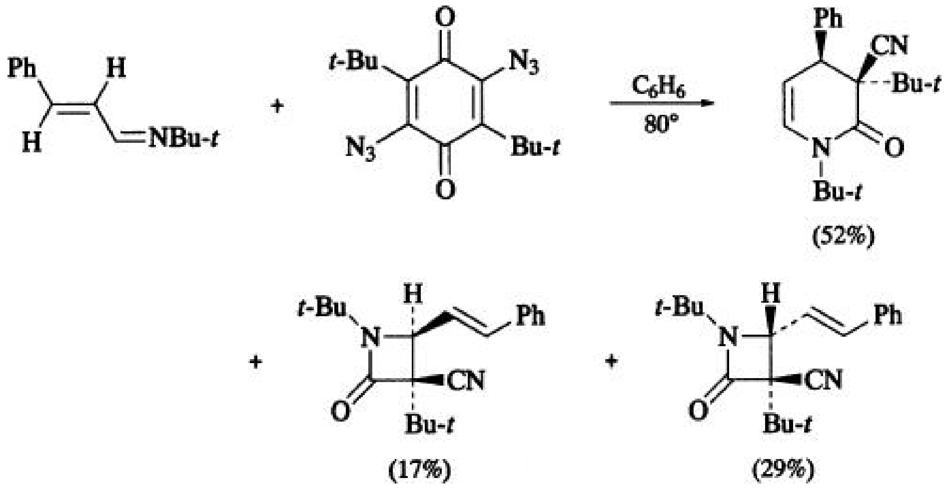
(148)

Reactions of this type have been studied with three distinct classes of substrates. Linear azadienes formed from cinnamaldehydes and anilines react with ketene and haloketenes to give 3,4-dihydro-2-pyridones in yields typically around 65% (Eq. 149). (241, 242)

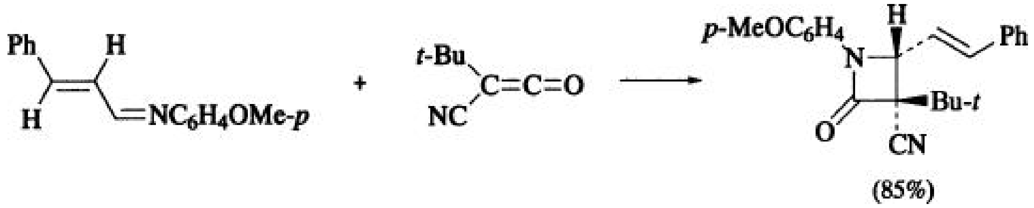


(149)

In the case of *tert*-butylcyanoketene generated from di-*tert*-butyldiazidoquinone in the presence of cinnamaldehyde-*tert*-butylimine, the *cis*-[4 + 2] adduct (52%) is accompanied by both *cis*- and *trans*-2-azetidinones (17% and 29%, respectively) (Eq. 150). (23) The ratio of [2 + 2] to [4 + 2] adducts in reactions of this type is controlled by the steric bulk on both the ketene and the azadiene; *tert*-butyl-cyanoketene and cinnamaldehyde *p*-methoxyaniline imine give only *trans*-azetidinone (Eq. 151). (23)

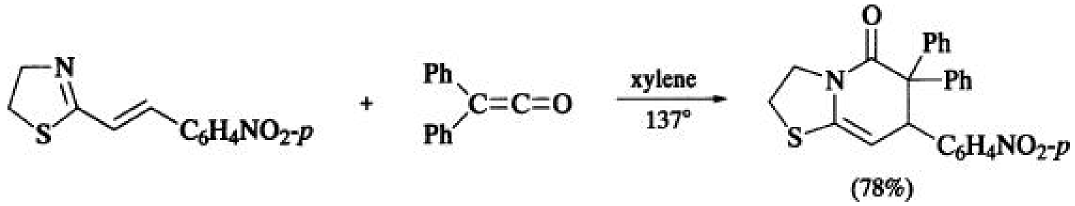


(150)



(151)

A second class of ketene-azadiene cycloadditions involves 2-styryl-4,5-dihydrothiazoles (Eq. 152), which react with diphenylketene to give thiazolopyridones in good yield. (243)



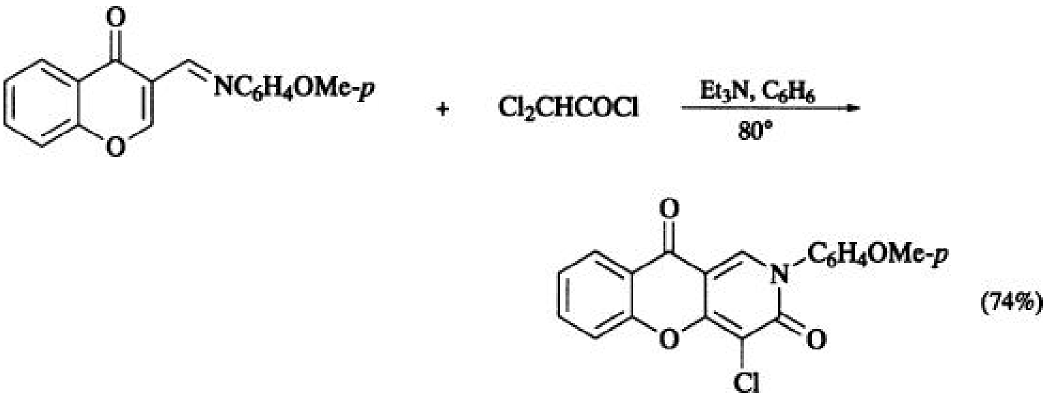
(152)

The third group of 1-azadiene-ketene [4 + 2] cycloadditions utilizes imines of chromone-3-aldehydes, which with dihalo- and haloarylketenes give good yields of pyrido(4,5-*b*)chromones (Eq. 153). Elimination of HCl in situ provides the additional unsaturation in the products. (244)

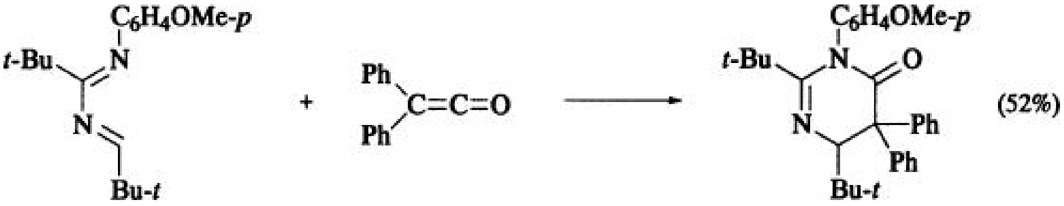
It would appear that considerable scope for further development lies with [4 + 2] cycloadditions of ketenes to azadienes.

3.3.1.3. Amidines

The addition of ketenes to amidines (1,3-diazadienes) results in [4 + 2] cycloaddition to form 5,6-dihydro-4-pyrimidones. Reaction of the amidine of Eq. 154 with diphenylketene, which results in a 52% yield of pyrimidone, is an example. (245)

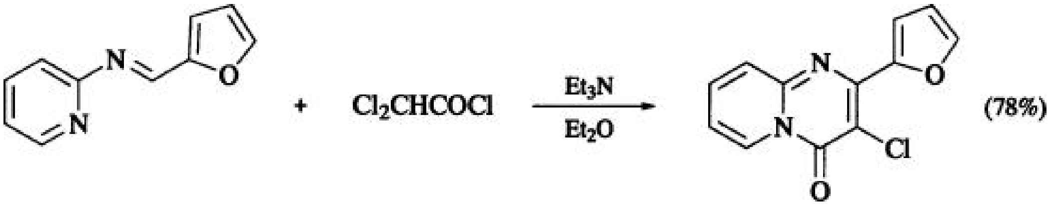


(153)



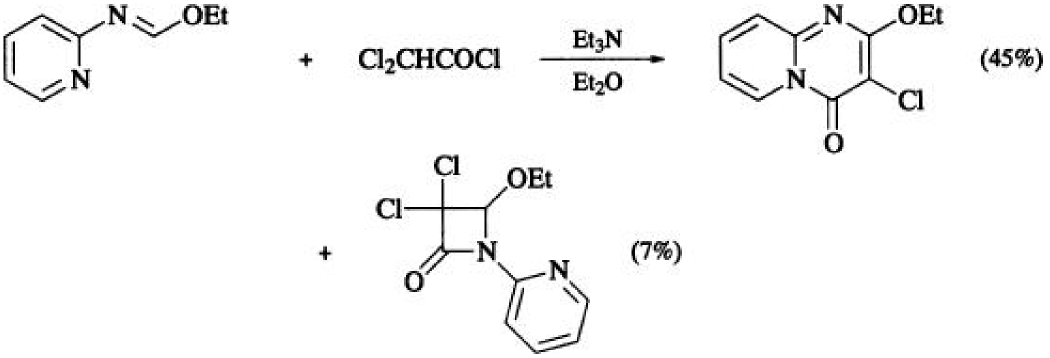
(154)

Cycloadditions of this type generally proceed in good yield; the orientation of addition is exclusively that leading to 4-pyrimidones. The alternative regiochemistry that would give dihydropyrimidine-5-ones has not been reported. Most recorded examples of this synthetically useful cycloaddition involve either ketenes or amidines bearing groups which may be eliminated to give 4-pyrimidones as the observed products. This process is typified by the reaction of furfuraldehyde 2-aminopyridineimine with dichloroketene, from which a 78% yield of a pyrido(1,2-*b*)pyrimidone is obtained (Eq. 155). (246)



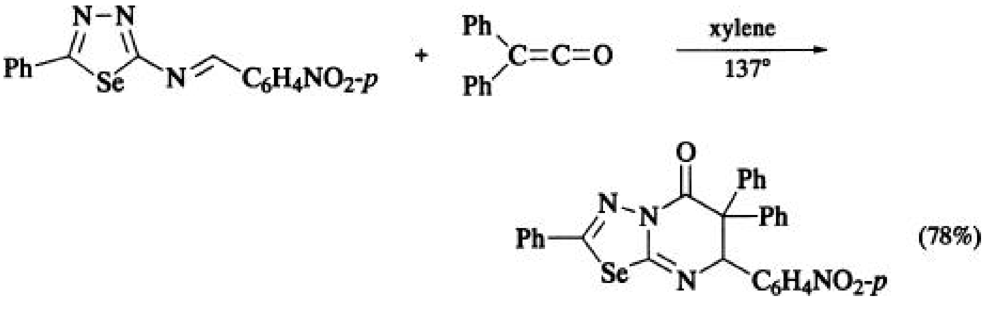
(155)

Few competing processes have been reported in these reactions. The only reference to byproducts arising from [2 + 2] cycloadditions is in the reaction of dichloroketene with imines derived from 2-aminopyridine: a 7% yield of β -lactam accompanied the 45% yield of pyrimidone (Eq. 156). (247)



(156)

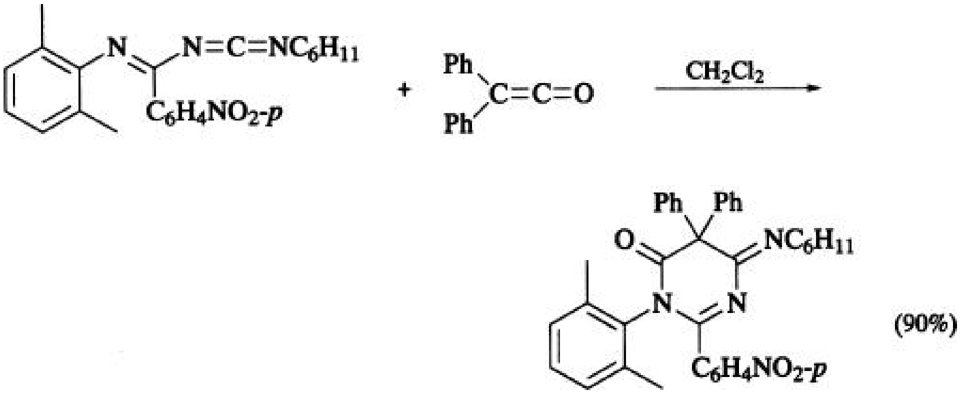
Although amidines made from 2-aminopyridines are used in most examples of this class of ketene cycloadditions, other 2-aminoheterocycles such as the selenadiazole in Eq. 157 provide good yields of the predicted products. (248)



(157)

It should also be noted that unusual amidines such as imine–carbodiimides

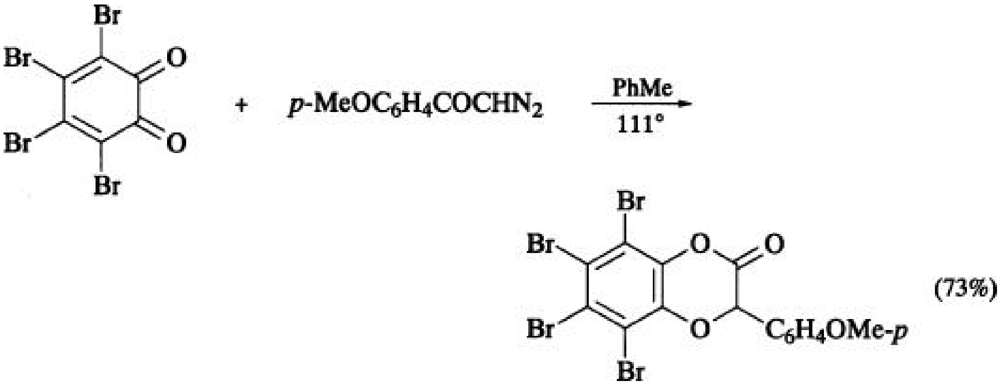
(Eq. 158) react with diphenylketene to give [4 + 2] adducts unaccompanied by 4-iminoazetidin-2-one byproducts. (249)



(158)

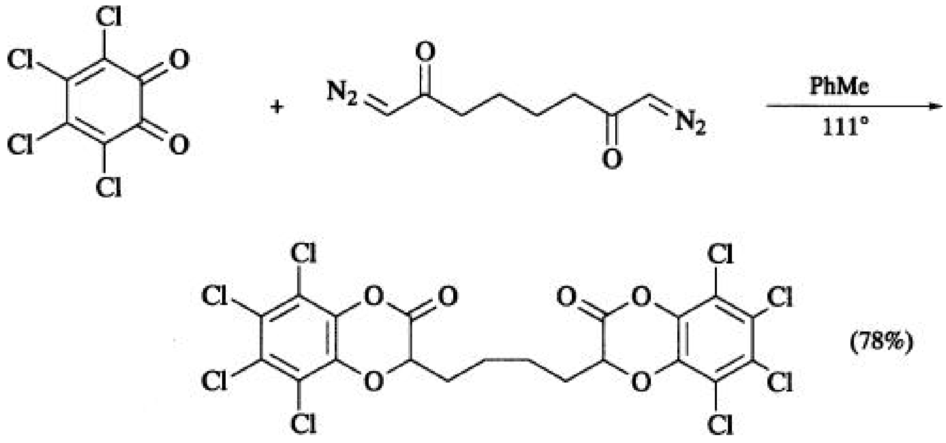
3.3.1.4. o-Quinones

o-Quinones undergo [4 + 2] cycloadditions with ketenes to give moderate to good yields of benzodioxenones. The addition of *p*-methoxy-phenylketene to tetrabromo-*o*-quinone to give a 73% yield of dioxenone (Eq. 159) is typical. (250)



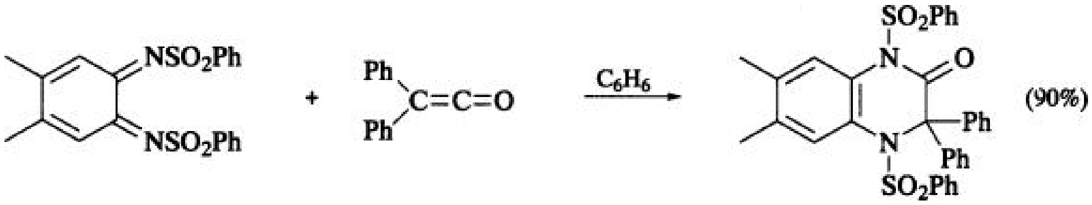
(159)

Several reactions involving double cycloaddition of tetrahalo-*o*-quinones to bis(ketenes) have been reported (Eq. 160). (250)

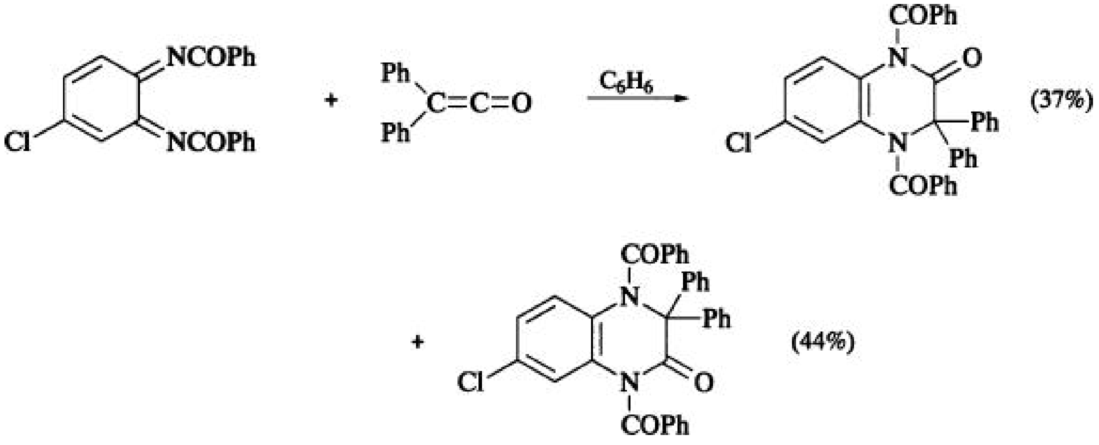


(160)

Analogous reactions with *o*-quinonimines give benzopiperidones (Eq. 161). (251) Some similar examples involve unsymmetrical quinonimines as in Eq. 162, and yield a mixture of the two possible cycloadducts. (251)



(161)

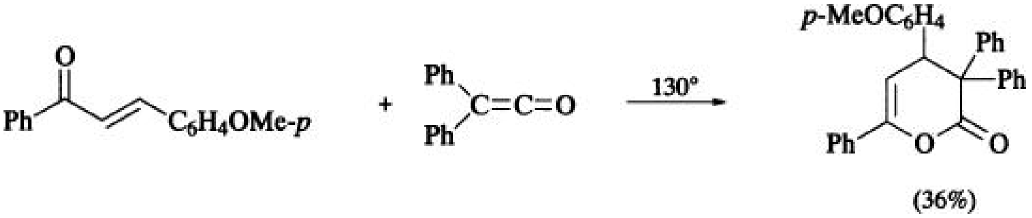


(162)

There appear to be no published examples of the [4 + 2] cycloaddition of ketenes to α -diketones.

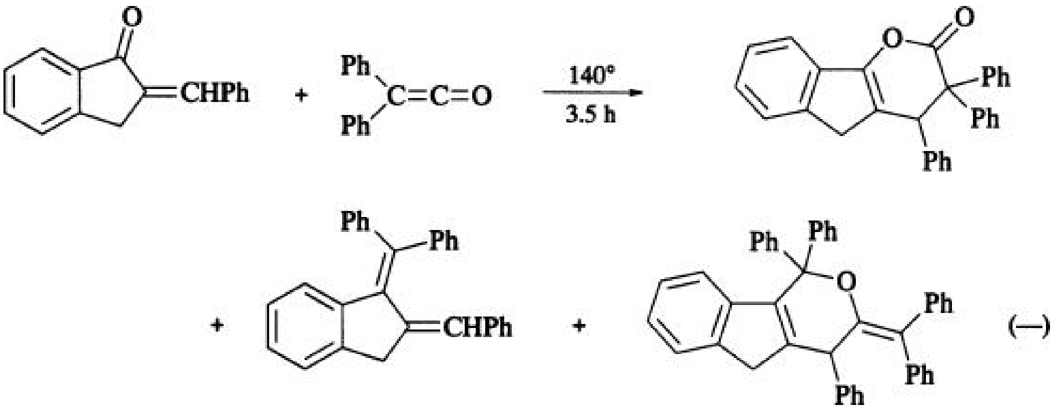
3.3.1.5. α , β -Unsaturated Ketones

Simple acyclic enones have seldom been reported to undergo [4 + 2] cycloadditions with ketenes; [2 + 2] addition to the carbonyl group to yield β -lactones or olefins is the general result of such reactions. The reaction of the enone in Eq. 163 with diphenylketene to give a 36% yield of product is one of the higher-yielding examples. (252)



(163)

In the reactions of benzylidenindanone and acenaphthone with diphenylketene, mixtures of cycloadducts are formed (Eq. 164). (253, 254)



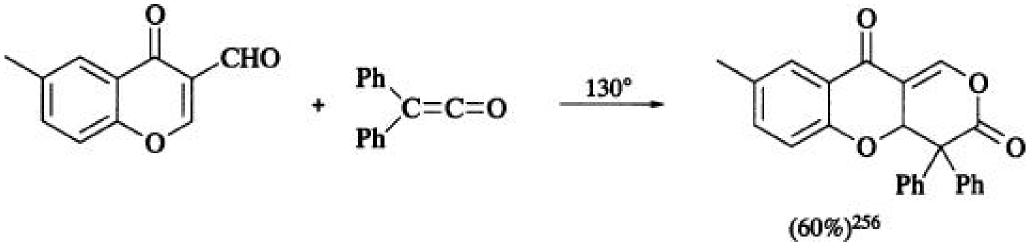
(164)

In contrast to these results, the interaction of ketenes with β -amino and β -alkoxy- α , β -unsaturated ketones (enaminoketones, vinylogous amides, and esters) gives rise to synthetically useful yields of lactones (2,3-dihydro-2-pyranones) arising from [4 + 2] cycloaddition. Well over 100 examples are recorded; the process, typified by the reaction of the enaminoketone in Eq. 165 with

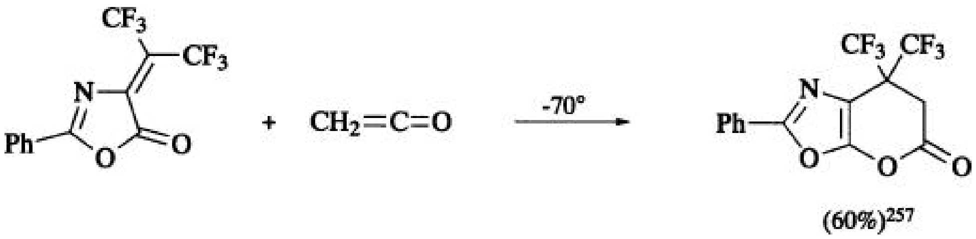
(165)

dichloroketene to give a lactone (92%), (255) can be carried out with various ketenes under mild conditions. Dichloroketene, ketene, and diphenylketene are most frequently employed.

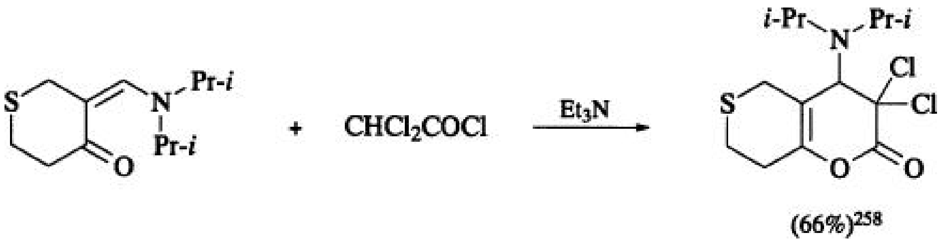
The scope of this cycloaddition can best be appreciated through examination of the examples in Eqs. 166–168. (256-258)



(166)

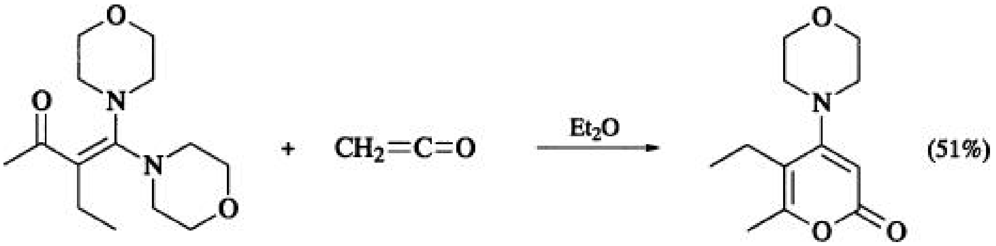


(167)



(168)

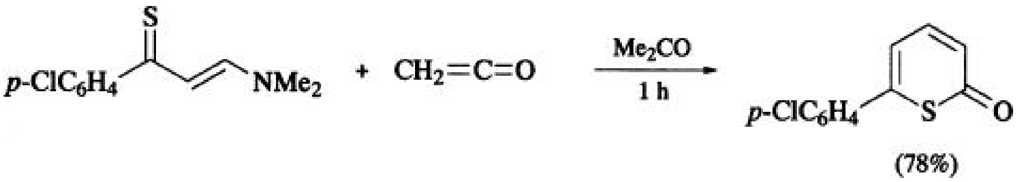
In the addition of ketene to β , β -diamino- α , β -unsaturated ketones, elimination of amine occurs in situ and the products are pyranones as illustrated in Eq. 169. (259)



(169)

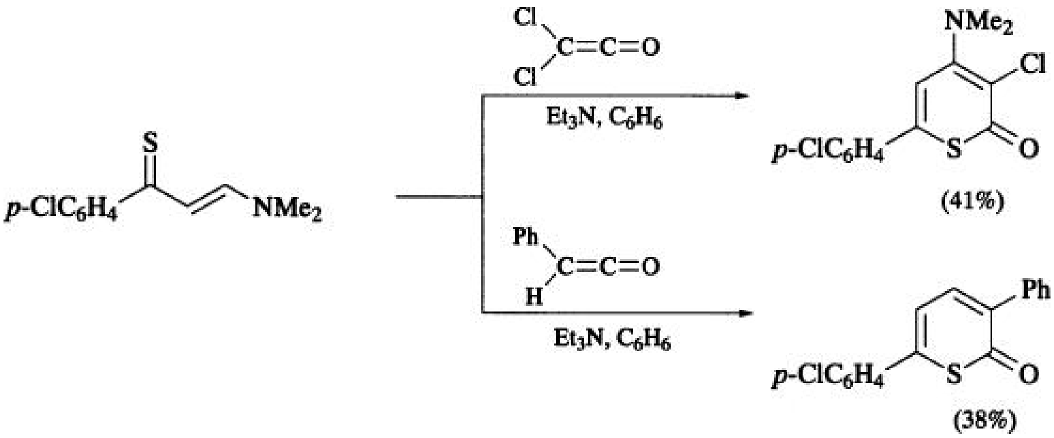
β -Unsaturated Thiones

In exact analogy to the enaminoketone cycloadditions described above, β -amino- α , β -unsaturated thiones (vinylogous thioamides) react with ketenes to give good yields of thiapyranones (Eq. 170). (260, 261)



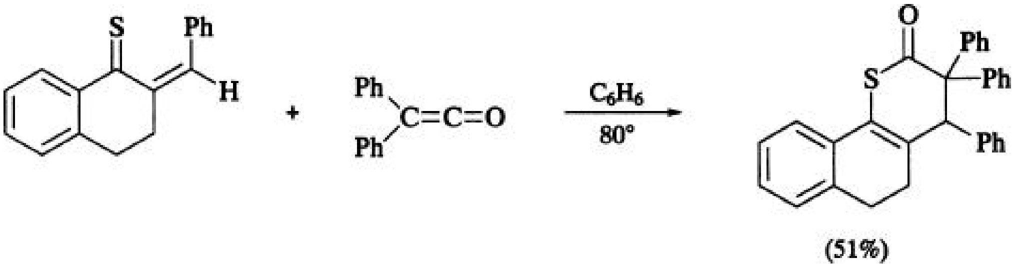
(170)

In all reported examples of this cycloaddition, in situ elimination of either amine from the enethione substrate or chlorine from dichloroketene gives rise to a fully unsaturated thiapyranone. Equation 171 shows that reaction of an α , β -unsaturated thione with a dichloroketene give chlorine elimination; the same thione reacts with phenylketene to afford deaminated product. (260)



(171)

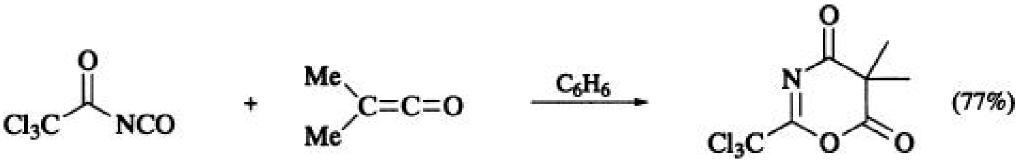
A few examples of the [4 + 2] cycloaddition of diphenylketene to simple unsaturated thiones have been reported; the preparation of the thiolactone in Eq. 172 (51 %) is typical. (262)



(172)

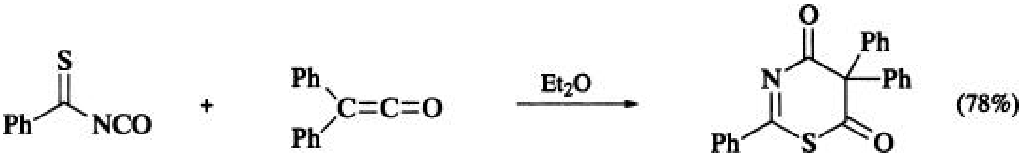
3.3.1.7. Acyl Isocyanates and Isothiocyanates

The reaction of ketenes with acyl isocyanates yields 1,3-oxazin-4,6-diones, as illustrated by the reaction of trichloroacetyl isocyanate and dimethylketene as in Eq. 173. (188) The analogous thiazinediones



(173)

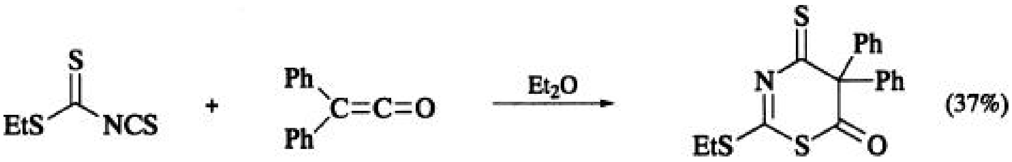
are formed when ketenes react with thioacyl isocyanates, as in the reaction of thiobenzoyl isocyanate with diphenylketene which gives 78% yield (Eq. 174). (263) These reactions are carried out in ether or aromatic solvents in the



(174)

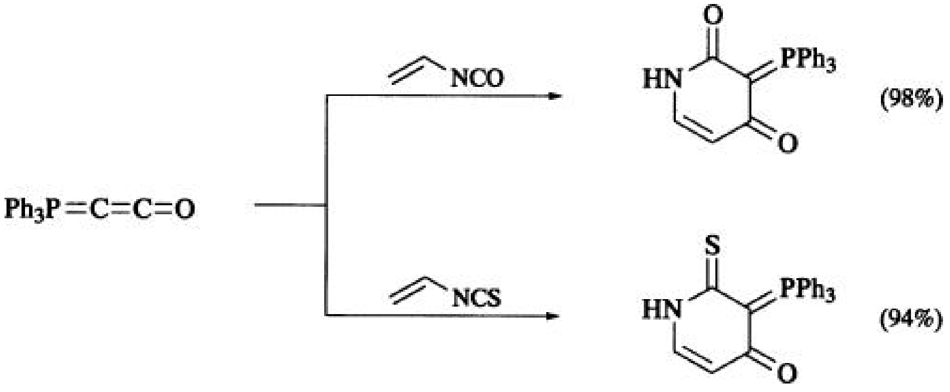
absence of catalysts. In no case has the isolation of azetidinedione byproducts been reported.

Acyl isothiocyanates exhibit similar chemistry with diphenylketene, yielding 1,3-thiazine-4-thion-6-ones (Eq. 175). (264, 265)



(175)

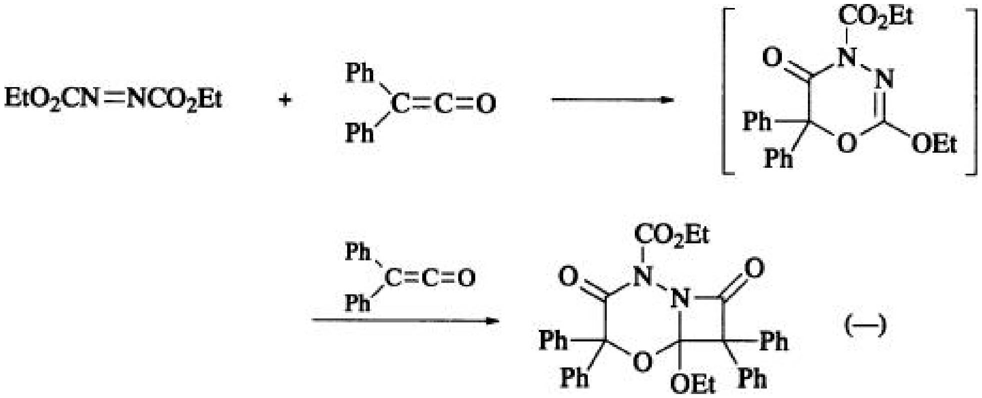
Vinyl isocyanate and isothiocyanate undergo [4 + 2] addition to triphenylphosphorane ketene (Eq. 176) to yield the corresponding phosphoranes. (266) Reaction of these isocyanates with the more common ketenes has not been reported.



(176)

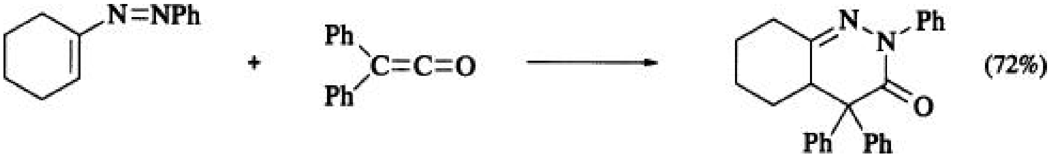
3.3.1.8. *Unsaturated and Acyl Azo Compounds*

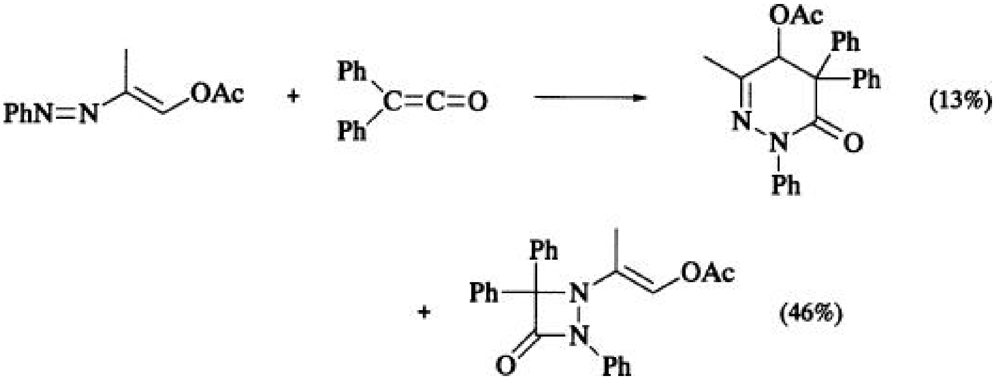
Diethyl azodicarboxylate and diphenylketene undergo a [4 + 2] cycloaddition, but the initial 1,3,4-oxadiazin-5-one product reacts with a second mole of ketene to give the final bicyclic product (Eq. 177). (267)



(177)

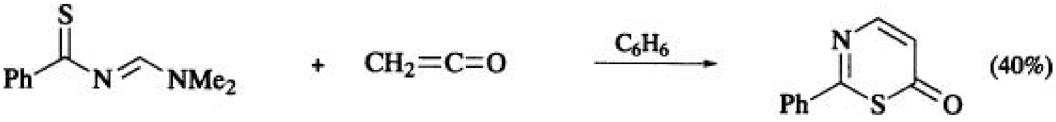
The unsaturated azo compound of Eq. 178 gives a 72% yield of diazine with diphenylketene, (268) but other unsaturated azo compounds give mixtures of [4 + 2] and [2 + 2] products (Eq. 179). (268)


(178)

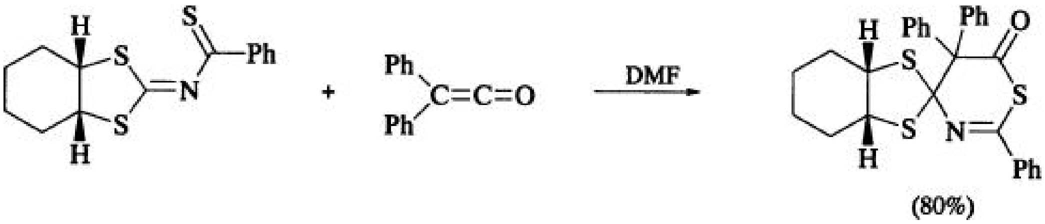

(179)

3.3.1.9. Thioacyl Imines

Ketene and phenylketene react with thioacyl imines to give moderate yields of 1,3-thiazin-6-ones, as illustrated by the reaction of ketene with the imine of Eq. 180 to give a single adduct (40%); elimination of a mole of dimethylamine occurs spontaneously to give this product. (269)


(180)

Another example of this reaction type is the production of a spirocyclic product (80%) from diphenylketene and the imine of Eq. 181. (270, 271)

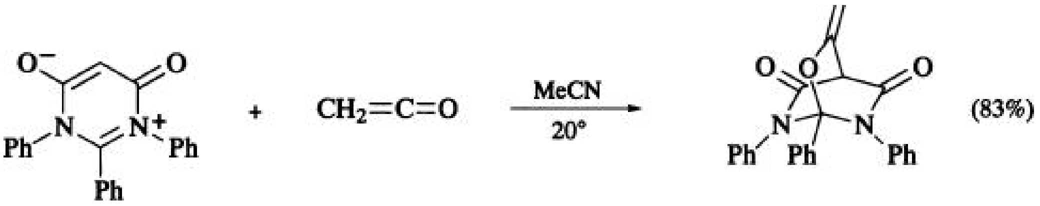

(181)

3.3.1.10. Mesoionic Compounds

In a rare example of what appears to be a 1,4-dipolar cycloaddition, 6-oxo-3,6-dihydro-1-pyridinium-4-olates react with the carbonyl moiety of various ketenes to give good yields of the bicyclic heterocycles (Eq. 182). (272) The extension of this reaction to other dipolarophiles has not been reported, but the process proceeds as illustrated with a wide variety of ketenes.

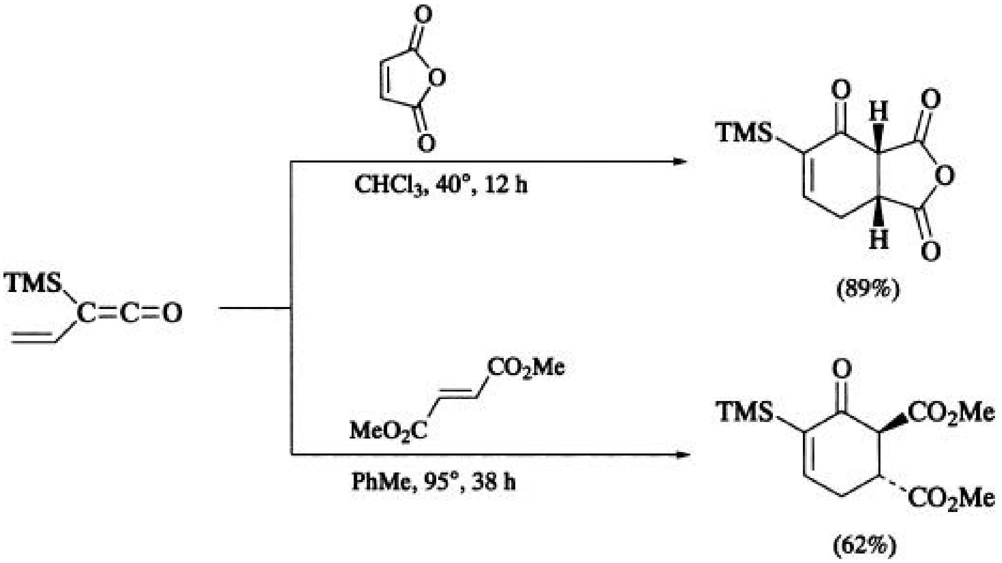
3.3.1.11. [4 + 2] Cycloadditions of Acyl- and Vinyl Ketenes to Olefins

Acyl- and vinylketenes undergo facile [4 + 2] cycloadditions with olefins bearing either electron-donating or electronegative substituents. Reactions with simple alkenes have not been reported. The products are cyclohexenones (from vinylketenes) and dihydropyran-4-ones (from acylketenes).



(182)

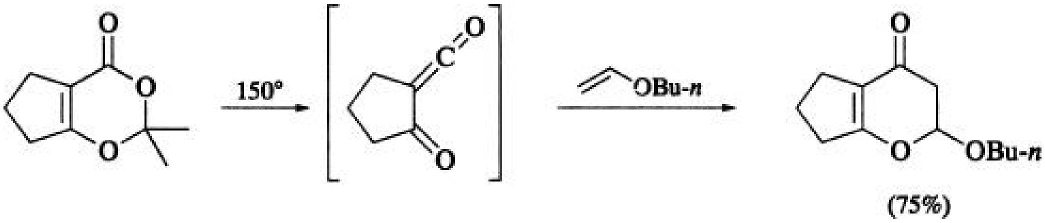
Electron-poor olefins such as maleic anhydride and dimethyl fumarate react with the silylvinylketene (Eq. 183) to give good yields of 2-cyclohexenones. (273)



(183)

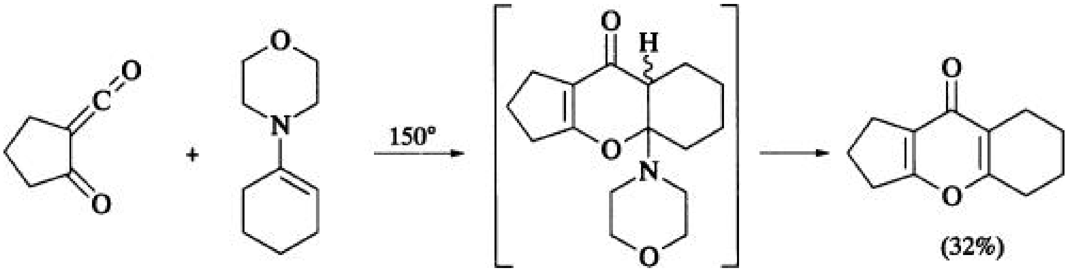
The stereochemistry of the products is that expected for typical Diels–Alder reactions. These promising results have not thus far been extended to other unsaturated ketenes.

Both acyl- and vinylketenes undergo [4 + 2] addition to enamines and enol ethers. Yields are generally good, as in the reaction of the acylketene from the dioxinone of Eq. 184 with butyl vinyl ether. (274, 275)



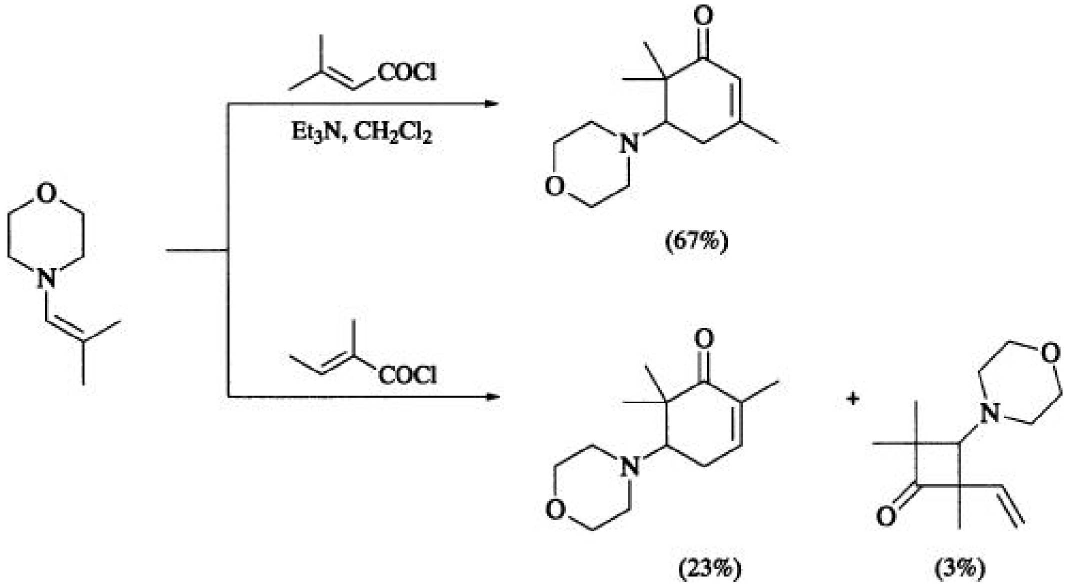
(184)

The same ketene reacts with cyclohexenylmorpholine to give a [4 + 2] product in 32% yield; the initially formed cycloadduct undergoes elimination of morpholine at the high temperature needed to generate the ketene (Eq. 185). (274)



(185)

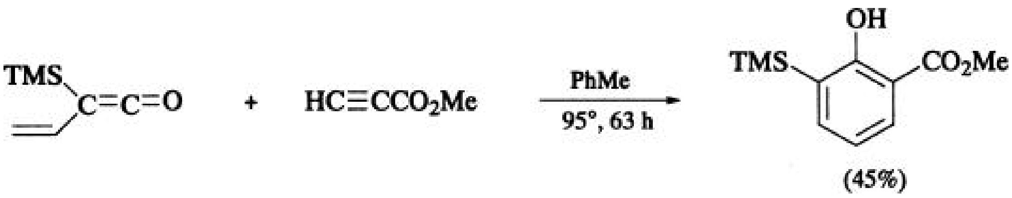
The formation of [2 + 2] cycloaddition byproducts has not been reported in the reaction of acylketenes with enamines, but when vinylketenes are allowed to react with enamines, mixtures of [2 + 2] and [4 + 2] cycloadducts sometimes occur. Thus while isobutenylmorpholine and the ketene from 3-methylbutenoyl chloride give only a [4 + 2] product (67%), use of the isomeric 2-methylketene leads to formation of both products (Eq. 186). (276)



(186)

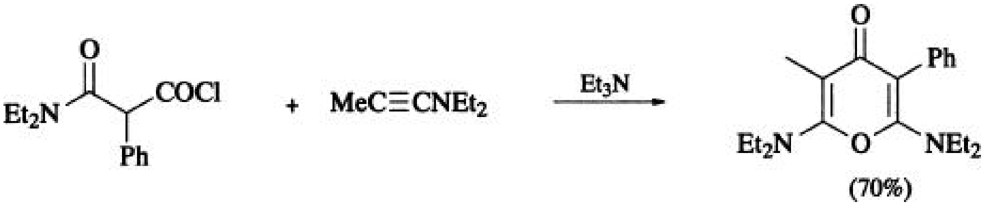
3.3.1.12. *[4 + 2] Cycloadditions of Acyl- and Vinylketenes to Acetylenes*

A few examples of this cycloaddition have been recorded. Vinyltrimethylsilylketene and electron-poor acetylenes such as methyl propiolate give moderate yields of phenols (Eq. 187). (273) A single example of an acylketene–benzyne cycloaddition is in the literature. (277)



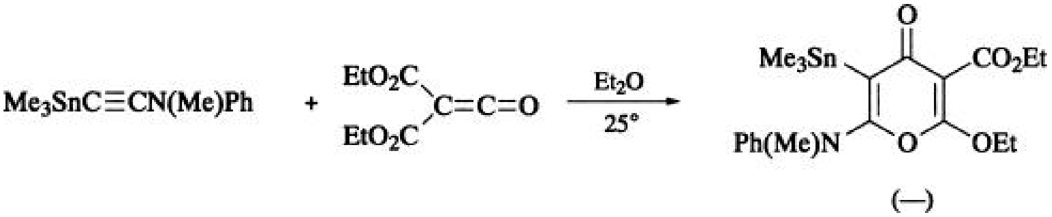
(187)

The other known acylketene–acetylene [4 + 2] cycloadditions all involve ynamines. Thus the ketene from the amido acid chloride in Eq. 188 reacts with 1-(diethylamino)propyne to give a 70% yield of the substituted 4-pyranone. (278)



(188)

A number of organometallic ynamines undergo [4 + 2] reaction with bis(carboethoxy)ketene to give pyranones (Eq. 189). (279) It would appear that the area of



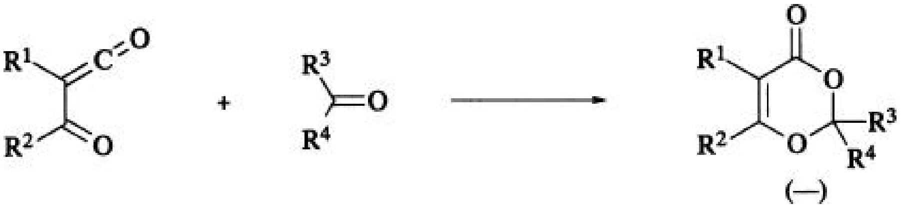
(189)

ketene–acetylene [4 + 2] cycloadditions is worthy of further exploration, for the reported examples of this reaction demonstrate the efficient assembly of highly functionalized phenols and heterocycles.

3.3.1.13. [4 + 2] Cycloaddition of Acyl- and Vinylketenes to Aldehydes and Ketones

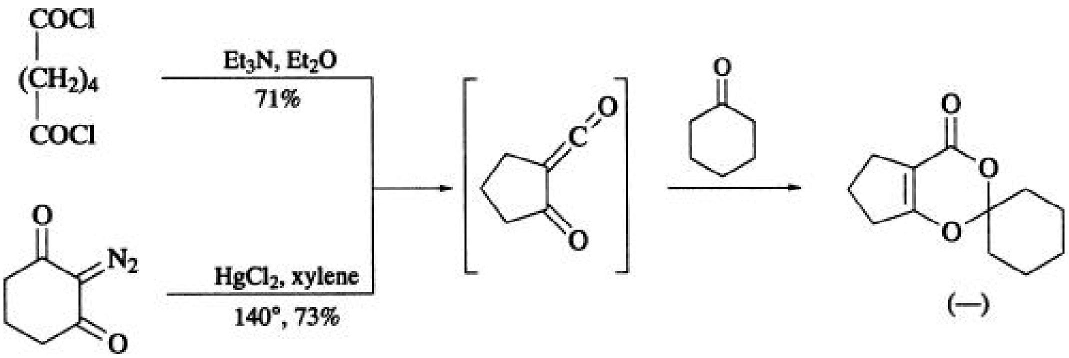
No examples of [4 + 2] cycloaddition of vinylketenes to aldehydes or ketones are in the literature, but a number of acyl ketenes do undergo such addition to give good yields of 1,3-dioxin-4-ones (Eq. 190). Byproducts arising from [2 + 2] additions do not appear in these reactions.

The greatest number of reported examples involve generation of the acylketene from adipoyl chloride in the presence of a carbonyl compound such as cyclohexanone; (280)



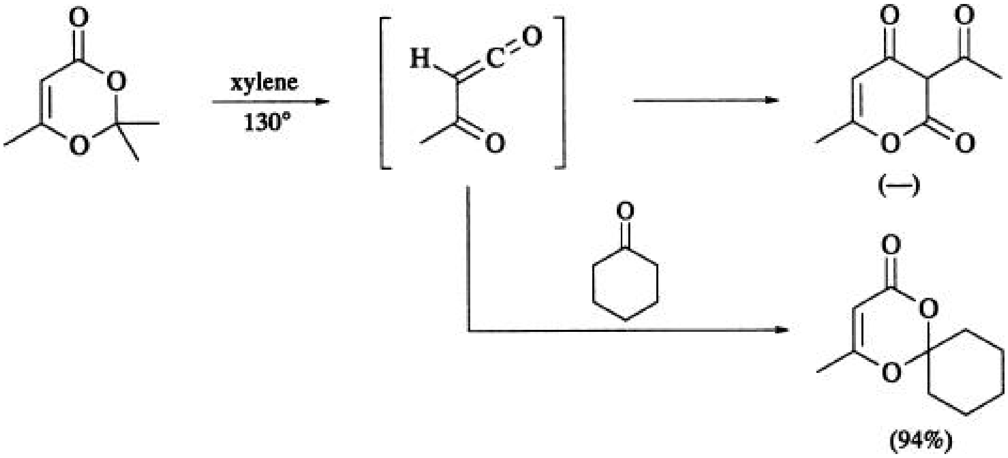
(190)

the same product is obtained in similar yield when the acylketene is generated from 2-diazocyclohexane-1,3-dione (Eq. 191). (280, 281)



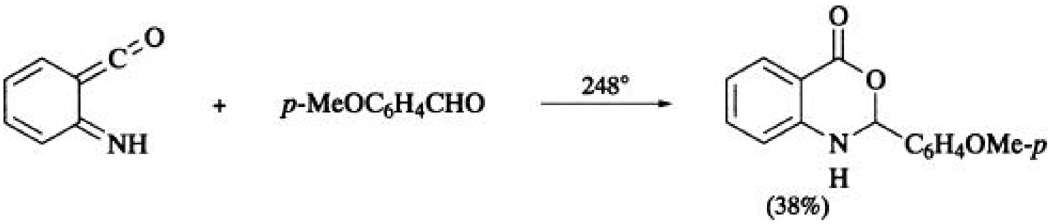
(191)

It should be noted that the 1,3-dioxinone products of this cycloaddition are themselves capable of undergoing retro [4 + 2] fragmentation to regenerate the acylketene, which in the absence of trapping agents will dimerize or decompose. Thus the commercially available 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one reverts to acetone and acetylketene above 100°; in the presence of cyclohexanone, a [4 + 2] adduct is formed in good yield. If no trapping agent is present, the dimer dehydroacetic acid is formed (Eq. 192). (282)



(192)

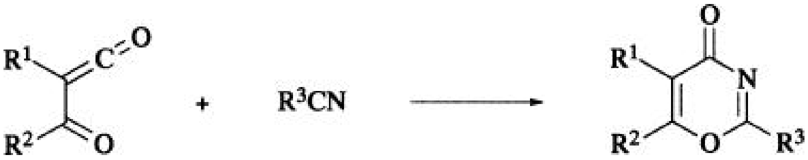
A single example of trapping an iminoketene with a benzaldehyde to give the benzoxazine ring is known (Eq. 193). (277)



(193)

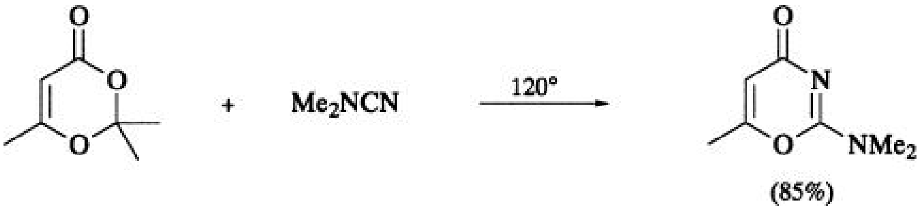
3.3.1.14. [4 + 2] Cycloaddition of Acylketenes to Nitriles and Cyanates

Nitriles, cyanamides, and cyanates participate in facile [4 + 2] cycloaddition reactions with acylketenes to yield derivatives of 1,3-oxazin-4-ones (Eq. 194).



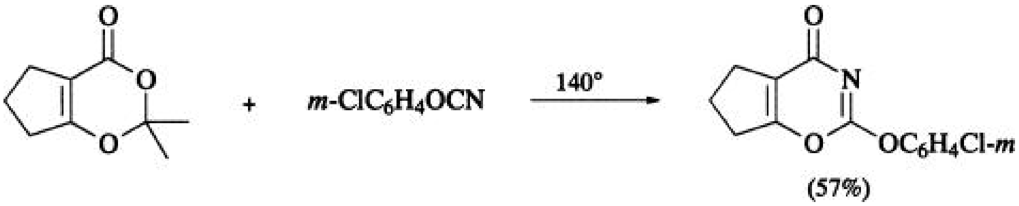
(194)

The requisite acylketenes are usually generated by cycloreversion of 1,3-dioxin-4-ones; the acetone byproduct is removed by distillation in the presence of the nitrile trapping agent. Thus the acetone–diketene adduct, when heated in the presence of dimethylcyanamide, provides an 85% yield of oxazinone (Eq. 195). (123, 274)



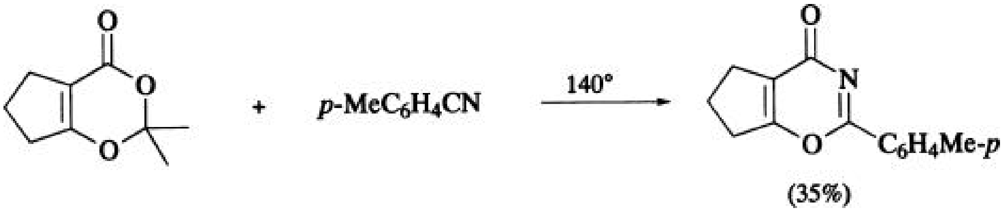
(195)

Similarly, a fused dioxinone and *m*-chlorophenyl cyanate react in boiling xylene to give a [4 + 2] adduct (57%) (Eq. 196). (123, 274)



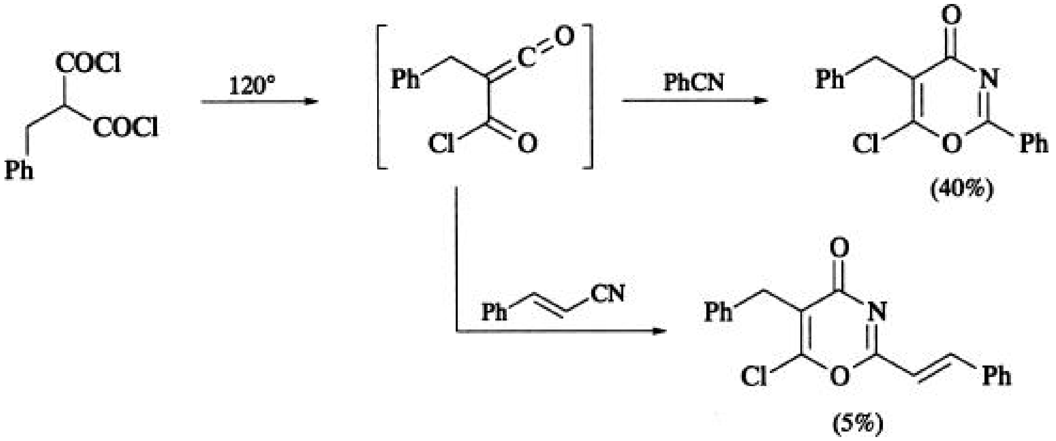
(196)

Yields of 1,3-oxazin-4-ones are generally greatest with cyanates and cyanamides. Most nitrile examples involve substituted benzonitriles and give yields in the range 30–50%. Thus *p*-tolunitrile and acylketene precursor at 140° give a 35% yield of the 2-aryl-1,3-oxazin-4-one (Eq. 197). (274)



(197)

The interesting chlorocarbonylketene from benzylmalonyl dichloride (Eq. 198) reacts with benzonitriles to give modest yields of 6-chloro-1,3-oxazin-4-ones. (283)

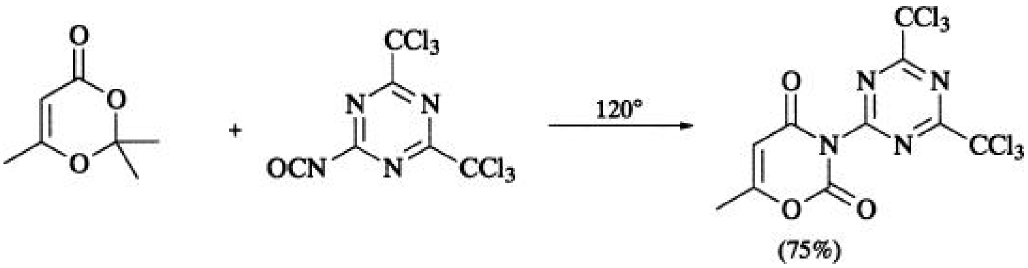


(198)

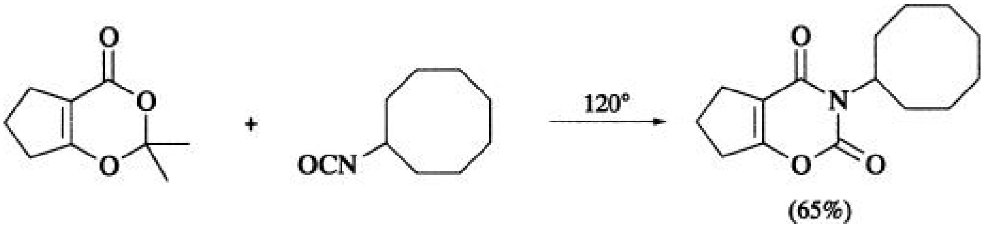
This ketene, combined with cinnamonitrile, gives a low yield of cycloadduct (Eq. 198). This is the sole example of a [4 + 2] cycloaddition of an acylketene to a nitrile other than a benzonitrile. (283)

3.3.1.15. [4 + 2] Cycloadditions of Acyl- and Vinylketenes to Heterocumulenes
Although no examples have been published of the cycloaddition of a vinylketene with a heterocumulene, there exist over 100 examples of [4 + 2] addition of acylketenes to isocyanates, isothiocyanates, carbodiimides, and *N*-sulfinylamines. These reactions lead to generally good yields of highly substituted 1,3-oxazines, 1,3-thiazines, and 1,2,3-oxathiazines.

The isocyanate system has been explored in greatest detail. When 1,3-dioxin-4-ones undergo cycloreversion to acylketenes in the presence of isocyanates, 1,3-oxazin-2,4-diones are produced in generally good yields. Typical examples include the generation of acetylketene from trimethyldioxinone in the presence of an isocyanate (Eq. 199) to give the [4 + 2] product in 75% yield; (274) an analogous reaction is shown in Eq. 200. (274)

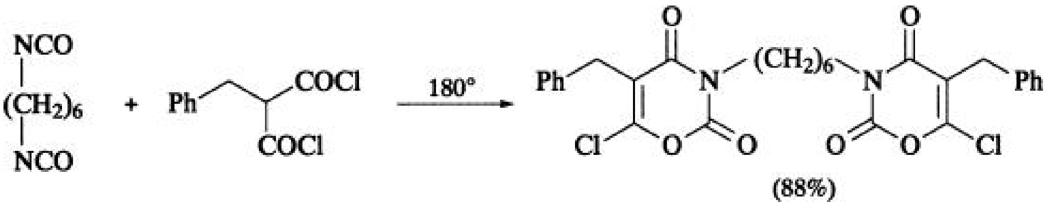


(199)



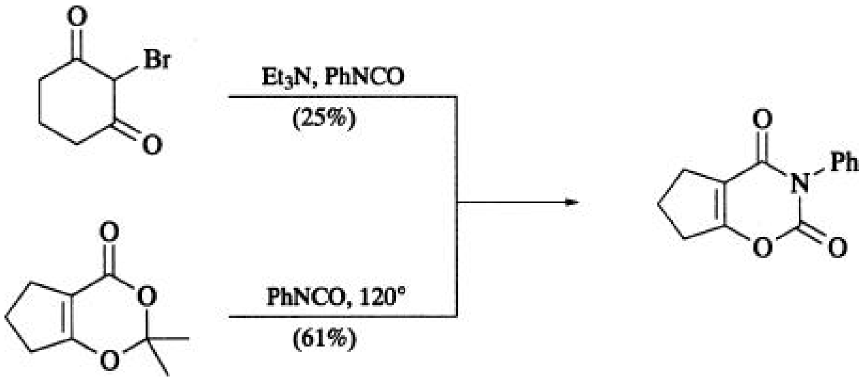
(200)

The requisite acylketenes can also be generated by pyrolysis of malonyl dichlorides, as in the preparation of a bis(oxazindione) in 88% yield (Eq. 201). (283)



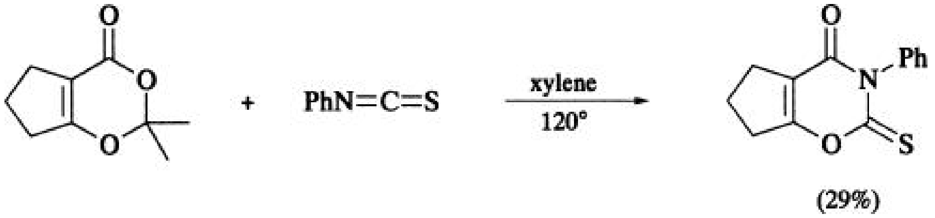
(201)

Isocyanate trapping of the acylketenes generated by Wolff rearrangement of 2-bromo-1,3-cyclohexanedione generally gives modest yields of [4 + 2] adducts; phenyl isocyanate provides only 25% yield. (284) When the 1,3-dioxin-4-one route to this ketene is used, the yield is 61% (Eq. 202). (274)



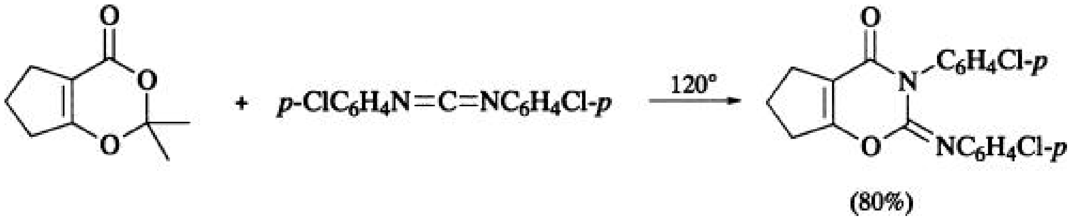
(202)

Isothiocyanate–acylketene reactions proceed in analogy to the isocyanate examples, but yields are generally poor. Thus phenyl isothiocyanate provides only a 29% yield of the [4 + 2] adduct (Eq. 203). (274)



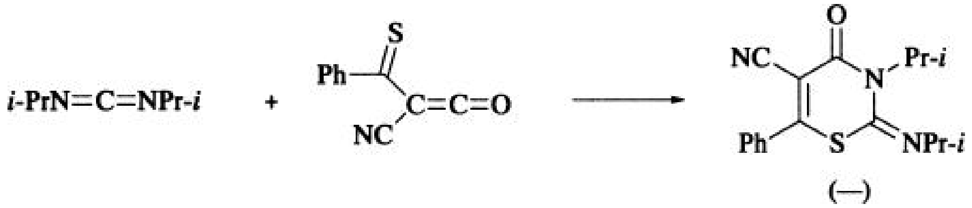
(203)

When a dioxinone is heated in the presence of carbodiimides (Eq. 204), excellent yields of 2-imino-1,3-oxazin-4-ones result. (274)

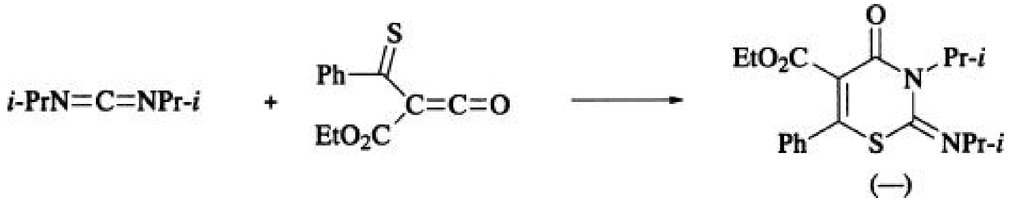


(204)

Interestingly, two multifunctional thioacylketenes react cleanly with diisopropylcarbodiimide (Eqs. 205 and 206). In both reactions the sole reported products



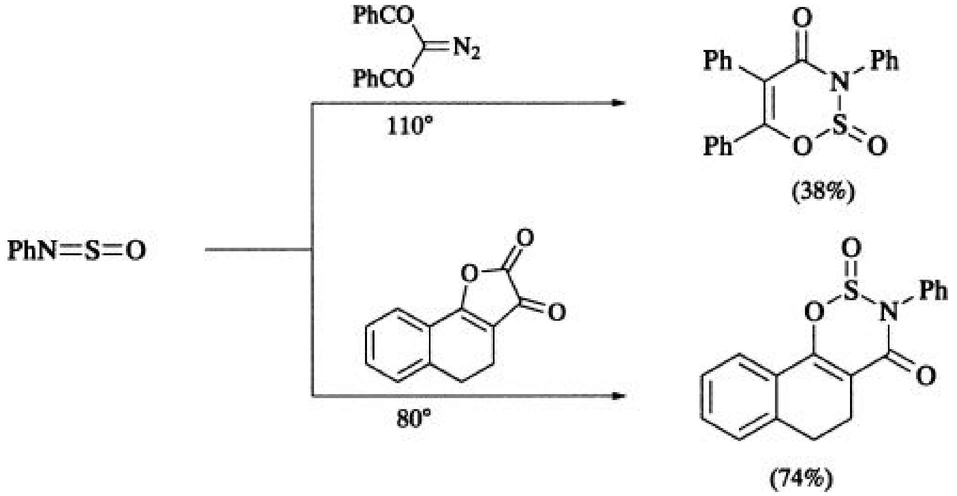
(205)



(206)

arise from [4 + 2] addition to the thioacylketene functionality; the other possible modes of reaction involving cyanoketene and carboethoxyketene groups are not seen. (285)

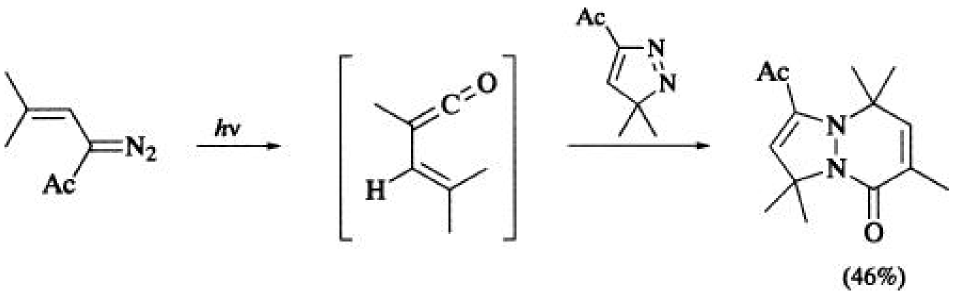
Decomposition of 2-diazo-1,3-diketones in the presence of *N*-sulfinylamines leads to modest yields of 1,2,3-oxathiazin-4-ones. Higher yields of this heterocyclic system are obtained when acylketenes are generated by thermal decarbonylation of dihydrofuran-2,3-diones: compare the reactions of dibenzoyl-diazomethane and naphthodihydrofurandione with *N*-phenyl-*N*-sulfinylamine to produce the corresponding cycloadducts in 38% and 74% yields, respectively (Eq. 207). (286, 287)



(207)

3.3.1.16. [4 + 2] Cycloaddition of Acyl- and Vinylketenes to Imines and Azo Compounds

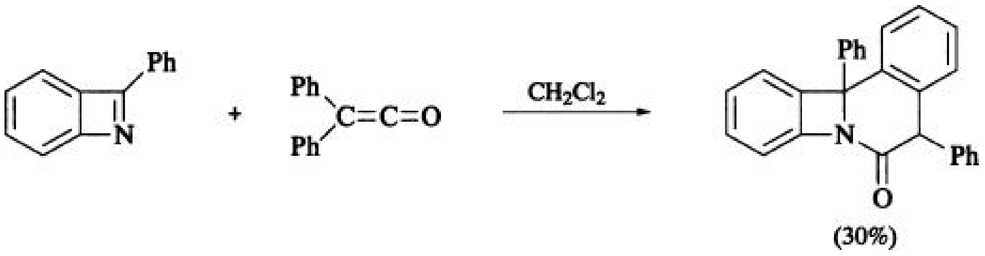
The methyl(dimethylvinyl)ketene formed upon irradiation of a parent diazoketone reacts with a diazacyclopentadiene to give the [4 + 2] adduct in 46% yield (Eq. 208). No products arising from cycloaddition to the olefin or carbonyl moieties of the diazo reactant are reported. (288) This is the sole literature example of a vinylketene-azo cycloaddition.



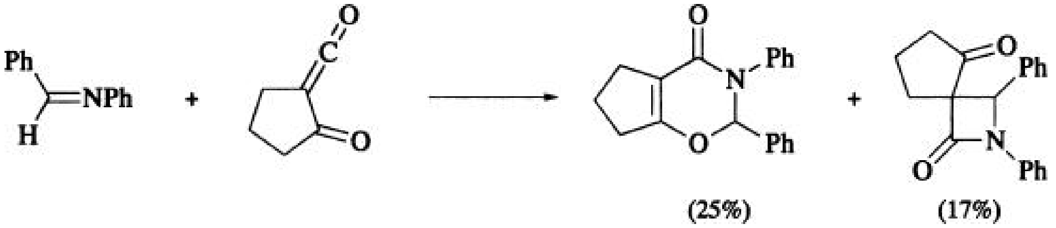
(208)

Imines undergo [4 + 2] cycloadditions with acylketenes but the reaction of diphenylketene with phenylbenzoazete to give the [4 + 2] adduct (30%) is the only reported reaction which could be considered a vinylketene–imine [4 + 2] cycloaddition (Eq. 209). (289)

Benzalaniline and an acylketene (Eq. 210) yield a mixture of [4 + 2] and [2 + 2] adducts. (281, 290) In all other reported cases, [4 + 2] cycloaddition occurs without

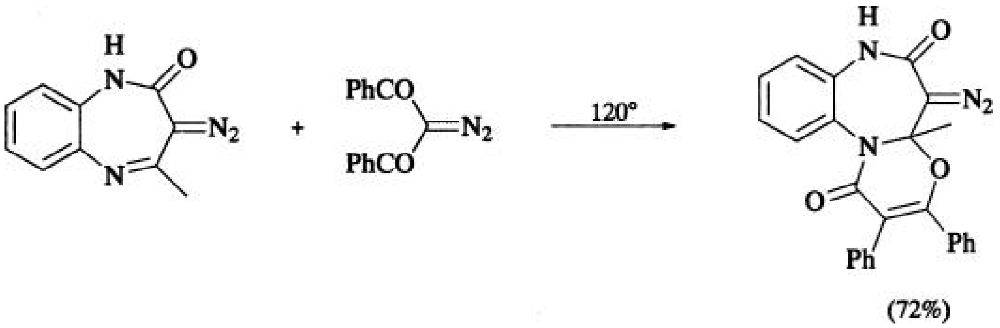


(209)



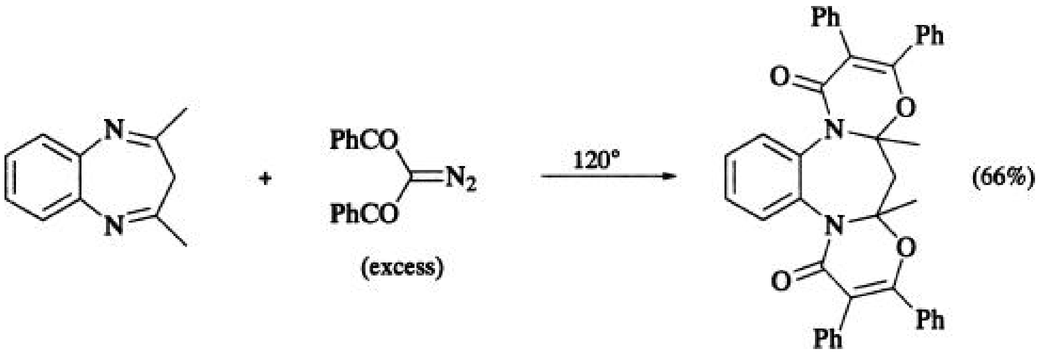
(210)

competing [2 + 2] reaction. The benzodiazepine of Eq. 211, for instance, gives a 72% yield of adduct when heated with dibenzoyldiazomethane, and double cycloaddition



(211)

of the same ketene to a suitable diazepine (Eq. 212) leads to a reasonable yield of adduct. (291)



(212)

4. Experimental Procedures

4.1. General

Cycloadditions with reactants that are liquids at room temperature are best performed by simply mixing the two reactants without solvent. If one of the reactants is gaseous, it is more convenient to use a solvent. The progress of the reaction can be estimated by disappearance of the characteristic yellow color of the ketene, by loss of the band at about 2100 cm^{-1} in the infrared spectrum, or by ^1H NMR spectroscopy. The product is often separated from the dimer and other byproducts by chromatography or distillation. Ketene, monoalkylketenes, and dimethylketene are usually allowed to react at or below room temperature, whereas the higher molecular weight ketenes can be heated to temperatures above 100°. The ketene is usually used in excess when dimerization is a major side reaction. Dichloroketene is generated and allowed to react in situ, generally in the presence of halide salts, as described below. The success of the reaction is often determined by the relative rates of cycloaddition and dimerization of the ketene. Although polar solvents and catalysts accelerate the cycloaddition, they are not of general utility since they also accelerate dimerization.

4.2. Safety

In general, cycloadditions with ketenes do not require facilities and special training not already possessed by those likely to work with such compounds. Good ventilation is essential, because concentrated ketenes, especially those of low molecular weight, are highly and exothermically reactive, especially with themselves, and have a sharp, overpowering odor. Alone among the ketenes (to our knowledge), dimethylketene forms a dangerously explosive addition product with oxygen. (292) Dimethylketene can be used on a large scale with appropriate precautions; in situ generation from the dimethylketene acylal of dimethylmalonic acid is a practical way to avoid this problem. (293, 294) Although oxidation of most other ketenes, (295) if it takes place at all, does not appear to generate explosive products, ketenes should be stored under nitrogen and precautions should be taken that are appropriate for compounds that form peroxides. Ketene itself can be stored neat for days at –78° (74) with some dimerization, but the monoalkylketenes, which can be prepared in concentrated form by pyrolysis of anhydrides, are exceedingly reactive. The dimerization of concentrated methylketene, even at –78°, may occur with such vigor as to vaporize the unreacted ketene with enough force to partially disassemble the apparatus. (110)

4.3. Preparation of Ketenes

Although early workers prepared ketene by the pyrolysis of acetone on the hot wire of a “ketene lamp,” (296) ketene is now best prepared in the laboratory by cracking commercially available diketene at atmospheric pressure in a hot tube, as described in a detailed procedure. (74) Ketene is prepared on an industrial scale by the pyrolysis of acetic acid. Mono- or dialkylketenes are made by dehydrohalogenation of an acid chloride with triethylamine in diethyl ether (297) or by dehalogenation of an α -halo acid halide with zinc or zinc–copper couple, as described below. The zinc dehalogenation method is applicable only to additions to olefins that are not susceptible to cationic polymerization. The zinc halide etherate formed in the reaction catalyzes the polymerization of olefins such as ethyl vinyl ether, styrene, furan, enol ethers, cyclopentadiene, and other conjugated dienes. (29) Various techniques described below have proven useful in sequestering the zinc salts and minimizing this problem. The more volatile alkylketenes are best prepared by pyrolyzing the corresponding anhydride in a hot tube, followed by bulb-to-bulb distillation to separate the ketene from carboxylic acid and uncracked anhydride. (56, 74) Dichloroketene, which is generated and used in situ, is prepared either by dehydrohalogenation of dichloroacetyl chloride or by reduction of trichloroacetyl chloride. Superior results are obtained, especially with hindered olefins, if phosphorus oxychloride is used to sequester the zinc chloride. (298) A more recent procedure recommends the use of 1,2-dimethoxyethane to suppress rearrangement of sensitive adducts of allylic ethers. (299) Ultrasonic irradiation is claimed to accelerate dichloroketene reactions, resulting in shorter reaction times, better yields, and the ability to use ordinary instead of activated zinc. The detailed preparation of ketene, (74) diphenylketene, (39) and *tert*-butylcyanoketene (300, 301) have been described. Less common, but valuable in specific cases, are ketene preparations by the pyrolysis of esters (302) (especially isopropylidene malonates; (293, 303, 304) thermal (305) or photochemical (306) ring opening of cyclobutenones; photorearrangement of 1-silyl-1,2-diones to yield silyloxyketenes; (307) pyrolysis of trimethylsilyloxyketene acetals; (308) photochemical cycloreversion of 9,10-bridged anthracenes; (309) cyanoketenes by the pyrolysis of 2,5-diazido-1,4-benzoquinones (23, 301) or 4-azido-2-furanones; (310-312) and the Wolff rearrangement of α -diazoketones. (313-315)

4.3.1.1. 2,2-Dimethyl-3-octylcyclobutanone (Preparation of Dimethylketene from the Dimethylketenacylal of Dimethylmalonic Acid) (316)

A mixture of 528 g (4 moles) of dimethylmalonic acid and 1623 g (16 moles) of acetic anhydride was heated slowly to boiling at a pressure of about 10 torr. The acetic acid formed was removed continuously over an efficient fractionating column. The removal of the theoretical amount of acetic acid from the reaction mixture was followed by spontaneous evolution of CO_2, as indicated by a rise in pressure. The evolution of CO_2 was allowed to continue at atmospheric pressure (vented apparatus) and was complete within a few hours. Removal of the excess acetic anhydride by vacuum distillation afforded 300 g (80%) of a crystalline residue of the dimethylketenacylal of dimethylmalonic acid; mp 80° (from petroleum ether).

A mixture of 9.2 g (0.05 mol) of the dimethylketenacylal of dimethylmalonic acid, 50 g (0.36 mol) of 1-decene, and 100 mg of potassium carbonate was heated slowly to 130°. The carbon dioxide formed was removed through a reflux condenser. The reaction was complete after 6 hours. Distillation of the mixture in vacuo afforded 14 g of 2,2-dimethyl-3-octylcyclobutanone (67% yield based on the dimethylketenacylal); bp 88° (1 mm).

4.3.1.2. 2,2-Dichloro-3,3,4-trimethylcyclobutanone (Dichloroketene via Zinc–Copper Dehalogenation of Trichloroacetyl Chloride in the Presence of Triethyl Phosphite) (317)

To a mixture of 10.0 g (155 mmol) of zinc–copper couple and 5.96 g (85 mmol) of 2-methyl-2-butene in 75 mL of dry ether, stirred under argon at room temperature, was added over 45 minutes to a solution of 24.44 g (134.4 mmol) of trichloroacetyl chloride and 20.56 g (134.1 mmol) of phosphorus oxychloride in 75 mL of dry ether. The mixture was stirred overnight after which the ether solution was separated from the precipitated zinc chloride and added to hexane, and the resulting mixture was partially concentrated under reduced pressure in order to complete precipitation of the chloride. The supernatant layer was decanted and washed successively with a cold aqueous solution of sodium bicarbonate, water, and brine and then dried over anhydrous sodium sulfate. Evaporation of the solvent under reduced pressure followed by distillation gave 13.35 g (87%) of 2,2-dichloro-3,3,4-trimethylcyclobutanone, bp 75° (2 mm); IR 1805, 1460, 1180, 870, 805, 745, 685 cm^{-1}.

4.3.1.3. 7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one [Dichloroketene (via Dehydrohalogenation of Dichloroacetyl Chloride with Triethylamine) and Cyclopentadiene] (318, 319)

To a vigorously stirred solution of 375 g (5.7 mol) of freshly distilled cyclopentadiene and 143.5 g (0.97 mol) of dichloroacetyl chloride was added 100 g (0.99 mol) of triethylamine over a period of 1.5 hours. After stirring for 15 hours under nitrogen, the mixture was filtered. Distillation afforded 124.3 g (72%) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one, bp 60–65° (2.5 mm); ^1H NMR ($CDCl_3$) δ 2.30–2.90 (m, 2H), 3.90–4.35 (m, 2H), 5.65–6.10 (m, 2H).

4.3.1.4. Bicyclo[3.2.0]hept-2-en-6-one. (Dechlorination of a 2,2-Dichlorocyclobutanone with Zinc/Acetic Acid) (318, 319)

To a vigorously stirred suspension of 261.7 g (4.00 mol) of zinc dust and 400 mL of glacial acetic acid was added dropwise at room temperature 124.3 g (0.70 mol) of 7,7-dichlorobicyclo[3.2.0]hept-2-en-6-one. After the addition was complete, the temperature was raised to and maintained at 70° for 40 minutes. The mixture was then cooled and treated with ether, and the zinc residue was removed by filtration. The ethereal layer was washed with a saturated solution of sodium carbonate to remove acetic acid and then dried with magnesium sulfate. Distillation afforded 61.5 g (81%) of bicyclo[3.2.0]hept-2-en-6-one, bp

60° (ca. 15 mm); ^{1}H NMR ($CDCl_3$) δ 2.30–2.80 (m, 3H), 3.10–3.55 (m, 2H), 3.65–3.95 (m, 1H), 5.60–5.85 (m, 2H).

4.3.1.5. 3-Ethoxy-2,2-dimethylcyclobutanone (Cycloaddition of Dimethylketene, Prepared from Isobutyric Anhydride, to a Vinyl Ether) (320, 321)

CAUTION: Dimethylketene reacts readily with oxygen to form an explosive peroxide, and it dimerizes readily to a solid product which may plug passageways in an experimental apparatus.

Isobutyric anhydride was passed under a slow stream of nitrogen into an electrically heated 16 × 76 mm glass tube. The vaporized anhydride was conducted to a Vycor glass tube, 15 mm in diameter and 46 cm long, heated electrically with Nichrome alloy ribbon (1100 W). Temperatures were measured with a thermowell which extended through the entire length of the Vycor pyrolysis chamber. Gaseous products from the pyrolysis chamber passed through an efficient water-jacketed copper condenser, and thence through two glass cyclone separators. The residual vapors were then passed through a trap held at 50°, and conducted to a cold condenser and receiver to collect the dimethylketene, bp 34°. With the pyrolysis tube at 500–525° and a nitrogen stream flowing at 1.5 cubic feet per hour, isobutyric anhydride was passed through the system at the rate of 2400 mL per hour. During a period of 45 minutes, 1710 g of anhydride was introduced and 144 g of dimethylketene was collected, corresponding to a conversion of 19%. (320) (The apparatus described for the cracking of diketene (74) is more clearly described than the one in the patent procedure above, and has been successfully used by the authors to prepare dimethylketene.)

To 960 g (13.3 mol) of ethyl vinyl ether, stirred at room temperature under a nitrogen atmosphere, 600 g (8.6 mol) of dimethylketene was added over a period of 4 hours. The mixture was stirred for several hours. Distillation through a 12-inch Vigreux column gave 315 g (4.4 mol) of unchanged ethyl vinyl ether and 975 g (80%) of 3-ethoxy-2,2-dimethylcyclobutanone, bp 82–183° (38 mm); ^{1}H NMR: δ 3.82 (t, 1H), 3.47 (q, 2H), 3.08 (d, 1H), 2.98 (d, 1H), 1.2 (t, 3H), 1.12 (s, 6H). (321)

4.3.1.6. 6-Methyl-2-oxa-1-phenyl-3,4-benzobicyclo[3.2.0]heptan-7-one (Intramolecular Cycloaddition) (322)

A solution of (*o*-propenylphenoxy)phenylacetic acid (1.2 g, 4.5 mmol) in benzene (50 mL) was added over 5 hours through a syringe to a solution of triethylamine (2.3 g, 22.5 mmol) and *p*-toluenesulfonyl chloride (1.7 g, 9 mmol) in benzene (50 mL) at reflux. After the addition was complete, the mixture was heated at reflux for 6 hours. Upon cooling, the mixture was washed with water (3 × 50 mL) and concentrated to about 30 mL. This concentrate was stirred with 3% aqueous sodium hydroxide solution (250 mL) for 10 hours to remove excess *p*-toluenesulfonyl chloride. The benzene layer was dried with magnesium sulfate and filtered, and the benzene evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (3% ethyl acetate in hexane) to give 0.9 g (83%) of 6-methyl-2-oxa-1-phenyl-3,4-benzobicyclo[3.2.0]heptan-7-one as a white solid, mp 95–96°; IR (neat) 1783, 1611, 1592 cm^{-1}. Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.40; H, 5.61.

4.3.1.7. 4,4-Dichloro-3-n-pentyl-2-cyclobuten-1-one (Cycloaddition of Dichloroketene to an Alkyne) (113)

In a flame-dried, 100-mL three-necked flask equipped with argon atmosphere, stirrer, reflux condenser, and constant pressure addition funnel was placed 0.40 g (18 mmol) of activated zinc, 0.576 g (6 mmol) of 1-heptyne, and 50 mL of anhydrous ether. To this stirred mixture was added dropwise over 1 hour a solution of 1.79 g (12 mmol) of phosphorus oxychloride (freshly distilled from potassium carbonate), trichloroacetyl chloride (12 mmol), and 10 mL of anhydrous ether. The mixture was then stirred at reflux for 4 hours and the residual zinc removed by filtration on a pad of Celite. The ether solution was washed with water, 5% sodium bicarbonate solution, and brine, and dried over potassium carbonate. After removal of ether under reduced pressure, the product was purified by bulb-to-bulb distillation at 100° bath temperature (0.1 mm), to give 1.08 g (90%) of the title compound as a clear oil. IR v_{max} (neat) 1800, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.12 (m, 1H, *J* = 2 Hz), 2.7 (t, 2H, *J* = 6 Hz), 2.0–0.7 (m, 9H). Anal. Calcd. for $C_9H_{13}Cl_2O$: C, 52.19; H, 5.85. Found: C, 52.10; H, 5.79.

4.3.1.8. 4-Ethyl-4-butyl-3-ethoxy-2-cyclobuten-1-one ([2 + 2] Cycloaddition of a Dialkylketene to an Acetylenic Ether) (124)

To a stirred solution of 51 g (0.73 mol) of ethoxyacetylene in 150 mL of hexane at room temperature was added 92 g (0.73 mol) of butylethylketene. Stirring was continued for 6 hours at room temperature, then the solution was heated under reflux overnight. Distillation through a 10-in. Vigreux column gave 73 g (51%) of pure product boiling at 88° (0.8 mm), n_D^{20} 1.4665.

4.3.1.9. 4-[2-(Ethylthio)propyl]-2-oxetanone ([2 + 2] Cycloaddition of Ketene to an Aldehyde) (323)

A solution of 38.6 g (0.288 mol) of 3-(ethylthio)butyraldehyde and 1.5 mL of boron trifluoride etherate in 350 mL of ether was stirred at room temperature. Ketene gas was added through a frit at such a rate that the reaction temperature could be maintained close to 20° by an external cold water bath. After 1.5 hours IR analysis of an aliquot showed all aldehyde to be consumed and a strong β -lactone carbonyl band to be present at 1818 cm^{-1}. The mixture was purged with nitrogen, washed with 25 mL of saturated aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and the ether removed under reduced pressure. Kugelrohr distillation (75–80°, 1.0 mm) gave

36.0 g (72%) of pure product. IR v_{max} (neat) 1818, 1110, 815 cm^{-1}; MS m/z 174 (calc, 174). Anal. Calcd. for $C_8H_{14}O_2S$: C, 55.1; H, 8.09. Found: C, 54.9; H, 8.14.

4.3.1.10. (R)-4-(1,1-Dichloroethyl)-2-oxetanone (Asymmetric Induction in [2 + 2] Cycloaddition of Ketene to an Aldehyde) (171)

A 250-mL three-neck flask was equipped with thermometer, ketene inlet tube, and stirrer and charged with a solution of 389 mg (1.2 mmol) of quinidine and 13.4 g (105 mmol) of 2,2-dichloropropionaldehyde in 150 mL of toluene. The mixture was stirred at –25° and about 1 equivalent of ketene was bubbled into the mixture at approximately 30 mmol/hour. After completion of the ketene addition, the mixture was warmed to room temperature and the catalyst was removed by washing with 3 × 30 mL of 4 N HCl. The mixture was dried over magnesium sulfate and toluene was evaporated under reduced pressure, leaving a residue that was purified by flash column chromatography (dichloromethane elution) and bulb-to-bulb distillation (90°, 0.5 mm) to give 16.2 g (96%) of product; $[\alpha]^{\mathrm{RT}}_{578} + 19.7°$. Crystallization from methylcyclohexane gave 12.5 g (77%) of optically pure product, $[\alpha]^{\mathrm{RT}}_{578} + 21.5°$(*c* = 1, cyclohexane), mp 51.1–51.2°. IR v_{max} (neat) 1845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.2 (3H, s), 3.6 (2H, d), 4.6 (1H, t). Anal. Calcd. for $C_5H_6O_2Cl_2$: C, 35.53; H, 3.58; Cl, 41.95. Found: C, 35.36; H, 3.57; Cl, 41.43.

4.3.1.11. α , α -Dichloro- β , β -bis(carboethoxy)propiolactone ([2 + 2] Cycloaddition of Dichloroketene to a Ketone) (324)

A solution of 27 g (0.15 mol) of diethyl mesoxalate and 45.5 g (0.32 mol) of dichloroacetyl chloride in 100 mL of absolute ether was stirred at 10° during the dropwise addition of 31.2 g (0.31 mol) of triethylamine. After 1 hour the solution was filtered and the filtrate stripped of ether. The residue was distilled to give 32.5 g (76%) of product of bp 120° (1.5 mm). IR v_{max} 1875 cm^{-1}. Anal. Calcd. for $C_9H_{10}Cl_2O_6$: C, 37.9; H, 3.8; Cl, 24.9. Found: C, 37.5; H, 3.6; Cl, 25.4.

4.3.1.12. 3,3-Dimethyl-2-(2-methyl-3H-naphtho[1,8-bc]thiophene-3-ylidene)butyronitrile (Olefin Synthesis by Reaction of a Ketene with a Ketone) (325)

A solution of 0.4 g (2 mmol) of 2-methyl-3*H*-naphtho[1,8-*bc*]thiophen-3-one and 0.302 g (1 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in 10 mL of dry benzene was heated at reflux in an argon atmosphere for 1 hour. The solvent was removed and the residue was chromatographed on a silica gel column with petroleum ether (bp 60–80°)/benzene (2:1). The major product recrystallized from hexane to give 0.209 g (75%) of product; mp 134°. IR v_{max} (KBr) 3030, 2970, 2860, 2160 cm^{-1}. ^{1}H NMR $CDCl_3$): δ 1.57 (s, 9H), 2.72 (s, 3H), 7.07 (d, 1H, J = 10 Hz), 7.45 (d, 1H, J = 10 Hz), 7.31–7.84 (m, 2H). Anal.

Calcd. for $C_{18}H_{17}NS$: C, 77.37; H, 6.13; N, 5.01; S, 11.47. Found: C, 77.17; H, 6.11; N, 5.06; S, 11.53.

4.3.1.13. N,N¢-Phenylenebis(2,2-diethylmalonamide) ([2 + 2] Cycloaddition of a Ketene to an Isocyanate) (188)

A solution of 8 g (0.05 mol) of *p*-phenylene diisocyanate and 14.7 g (0.15 mol) of diethylketene in 100 mL of toluene was heated in a sealed tube at 180° for 18 hours. The reaction mixture was then evaporated to dryness and the solid crude product was washed with cyclohexane to give 16.3 g (91%) of product; mp 130° from ethanol. IR (CCl_4) ν_{max} 1748 cm^{-1}.

4.3.1.14. 1,2-Di(m-methoxyphenyl)-4,4-diphenyl-1,2-diazetidinone ([2 + 2] Cycloaddition of a Ketene to an Azo Compound) (201)

A solution of 0.61 g (2.5 mmol) of 3,3¢-dimethoxyazobenzene and 0.51 g (2.5 mmol) of diphenylketene in 100 mL of benzene was irradiated for 0.3 hour through Pyrex with a General Electric Uviarc UA-3 lamp. Removal of benzene left a glassy residue that was extracted with four 50-mL portions of boiling hexane. Recrystallization of the residue from ethanol gave 0.72 g (69%) of product; mp 103–106°. IR ν_{max} 1780 cm^{-1}. Anal. Calcd. for $C_{28}H_{24}N_2O_3$: C, 77.04; H, 5.54. Found: C, 76.92; H, 5.55.

4.3.1.15. 5-Diphenylmethylene-2,4-di-tert-butyl-1,3-oxathiolane ([3 + 2] Cycloaddition to Diphenylketene) (326)

A solution of 1.80 g (9 mmol) of *trans*-2,5-di-*tert*-butyl-1,3,4-thiadiazoline and diphenylketene (2.10 g, 10.8 mmol) in 20 mL of methylcyclohexane was heated at reflux for 5 hours. After removal of solvent, the crude product was chromatographed over 100 g of silica gel using benzene as eluant to afford 3.11 g (94%) of 5-diphenylmethylene-2,4-di-*tert*-butyl-1,3-oxathiolane, mp 120–123°; IR (KBr) 1630, 1030, 1010, 700, 695 cm^{-1}. Anal. Calcd. for $C_{24}H_{30}OS$: C, 78.63; H, 8.27; S, 8.75. Found: C, 78.64; H, 8.26; S, 8.81.

4.3.1.16. 3,6-Dihydro-2-[trifluoro-1-(trifluoromethyl)ethylidene]-2H-pyran ([4 + 2] Cycloaddition of Ketene to a Diene) (231)

A mixture of 10.5 g (59 mmol) of bis(trifluoromethyl)ketene, 3.2 g (59 mmol) of 1,4-butadiene, and 0.01 g of hydroquinone was heated at 70° in a sealed ampule for 35 hours. Distillation of the reaction mixture yielded 12.5 g (90%) of the pyran product, bp 76–78° (15 mm). IR ν_{max} (neat) 1628 cm^{-1}; ^{19}F NMR (CCl_4) δ 56.5 (q, *J* = 9.9 Hz), 59.8 (q, *J* = 9.9 Hz). ^1H NMR (CCl_4) δ 3.25 (m, 2H), 4.74 (m, 2H), 6.10 (m, 2H). Anal. Calcd. for $C_8H_6F_6O$: C, 41.4; H, 2.58. Found: C, 41.7; H, 2.64.

4.3.1.17. 2-(p-Methoxyphenyl)-4-chloro-8-methyl[1]benzopyrano[3,2-c]pyridin-3,1(2H)-dione ([4 + 2] Cycloaddition of a Ketene to a 1-Azadiene) (244)

To a solution of 0.789 g (3 mmol) of 6-methyl-3-(*p*-methoxyphenyliminomethyl)chromone and 0.91 g (9 mmol) of triethylamine in 200 mL of dry benzene heated at reflux was added a solution of 0.88 g (6 mmol) of dichloroacetyl chloride in benzene. The mixture was cooled and filtered, and the filtrate was retained. The residue was slurried with water to remove triethylamine hydrochloride and the resulting product was dried and added to that obtained by evaporating the benzene filtrate. The combined crude product was recrystallized from anisole to give 0.79 g (72%) of the title compound, mp 318°. Anal. Calcd. for $C_{20}H_{14}ClNO_4$: C, 65.3; H, 3.8; N, 3.8. Found: C, 65.7; H, 3.5; N, 3.8.

4.3.1.18. 3-Chloro-2-ethoxy-9-methylpyrido[1,2- α]pyrimidin-4(4H)-one ([4 + 2] Cycloaddition of a Ketene to an Amidine) (247)

A solution of 3.54 g (24 mmol) of dichloroacetyl chloride in 19 mL of dry 1,2-dimethoxyethane was added dropwise to a solution of 3.28 g (20 mmol) of ethyl *N*-(3-methyl-2-pyridyl)formimidate and 4.85 g (48 mmol) of triethylamine in 40 mL of dry dimethoxyethane with stirring at –15°. The mixture was then stirred for 5 hours at room temperature. Removal of the solvent under vacuum gave a residue that was dissolved in 100 mL of dichloromethane, washed with water, dried over sodium sulfate, and concentrated under vacuum. The residue was subjected to chromatography over 150 g of silica gel; elution with 2:1 hexane:ethyl acetate gave 3.85 g (80%) of the title compound, mp 165–166° (recrystallized from benzene). IR ν_{max} ($CHCl_3$) 1675, 1635 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.50 (t, 3H), 4.60 (q, 2H), 8.97 (1H, dd). Anal. Calcd. for $C_{11}H_{11}ClN_2O_2$: C, 55.35; H, 4.65; N, 11.74. Found: C, 55.36; H, 4.60; N, 11.71.

4.3.1.19. 3,3-Diphenyl-4-methoxy-3,4,5,6-tetrahydro-2H-naphtho[2,1-e]pyran-2-one ([4 + 2] Cycloaddition of a Ketene to an Enone) (327)

A mixture of 1.1 g (5.67 mmol) of freshly distilled diphenylketene and 1.07 g (5.67 mmol) of β -methoxymethylene)- α -tetralone was heated at 82° until the IR spectrum of the mixture disclosed loss of the 2100 cm^{-1} ketene band. The mixture was allowed to cool to about 50° and 5–7 mL of petroleum ether was added. The resulting crystalline product was recrystallized from benzene/hexane to give 1.78 g (82%) of the pyranone, mp 161–162°. IR ν_{max} (neat) 1760, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.30–2.85 (br, 4H), 3.10 (s, 3H), 4.20 (s, 1H), 7.21 (s, 10H). Anal. Calcd. for $C_{26}H_{22}O_3$: C, 81.68; H, 5.76. Found: C, 81.50; H, 5.81.

4.3.1.20. 3-(p-Chlorophenyl)-3,4-dihydro-6-methyl-2H-1,3-oxazine-2,4-dione ([4 + 2] Cycloaddition of an Acylketene to an Isocyanate) (274)

A stirred mixture of 28.4 g (0.2 mol) of 2,2,4-trimethyl-1,3-dioxin-4-one and 38.3 g (0.25 mol) of *p*-chlorophenyl isocyanate was heated at 120–130° for 15–20 minutes while the acetone formed was removed by distillation. The cooled residue was triturated with petroleum ether and the crude product was recrystallized from methanol to give 40.4 g (85%) of product; mp 215–217°. Anal. Calcd. for $C_{11}H_8ClNO_3$: C, 55.7; H, 3.4; N, 5.9; Cl, 14.9. Found: C, 55.7, H, 3.4; N, 6.2; Cl, 14.7.

5. Tabular Survey

The search of published literature for ketene cycloadditions extends to the end of 1988, and a few later papers are cited. The patent literature search covers the same period, but the authors have included examples only from patents which in our experience or judgment ought to be reproducible.

There are a few entries in the tables for which it could be argued that the involvement of a free ketene reactant is unproven or even unlikely. Our basis for including such entries is that the reaction products are predictable if one assumes a ketene intermediate; whether or not a free ketene has a finite existence under the reaction conditions is of secondary importance to most preparative chemists.

A number of reaction starting material and product structures show a particular geometry of olefinic substitution. The reader should be aware that the original literature does not in every case rigorously establish such geometry; thus the original papers should be read critically by readers for whom this is an important point.

The tables follow the order of discussion in the Scope and Limitations section. Within each table, compounds reacting with ketenes are listed according to increasing carbon number, and increasing hydrogen number within a given carbon number. Carbon(s) and hydrogens residing in ester, ether, silyl ether, alkylamine, and other pendant groups are counted except in those cases where the availability of a series of closely homologous reactants allows creation of a subtable within a table. Yields are given in parentheses; a dash in the appropriate column indicates that yield(s) or reaction conditions were not reported.

The following abbreviations appear in the tables:

Ac	acetyl
Bn	benzyl
Bu	butyl
DMF	*N,N*-dimethylformamide
Et	ethyl
Me	methyl
Ph	phenyl
Pht	*o*-phthalyl
Pr	propyl

TBDMS	*tert*-butyldimethylsilyl
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl

Table I. Ketene Dimers

View PDF

Table II. Mixed Ketene Dimers

View PDF

Table III. [2 + 2] Cycloaddition of Ketenes to Acyclic Olefins

View PDF

Table IV. [2 + 2] Cycloaddition of Ketenes to Cyclic Olefins

View PDF

Table V. [2 + 2] Cycloaddition of Ketenes to Acyclic Dienes

View PDF

Table VI. [2 + 2] Cycloaddition of Ketenes to Cyclic Dienes

View PDF

Table VII. [2 + 2] Cycloaddition of Ketenes to Arenes

View PDF

Table VIII. [2 + 2] Cycloaddition of Ketenes to Allenes

View PDF

Table IX. [2 + 2] Cycloaddition of Ketenes to Enamines

View PDF

Table X. [2 + 2] Cycloaddition of Ketenes to Enol Ethers

View PDF

Table XI. [2 + 2] Cycloaddition of Ketenes to Enol Carboxylates

View PDF

Table XII. [2 + 2] Cycloaddition of Ketenes to Polyoxygenated Olefins

View PDF

Table XIII. Intramolecular Cycloadditions

View PDF

Table XIV. [2 + 2] Cycloaddition of Ketenes to Alkynes

View PDF

Table XV. [2 + 2] Cycloaddition of Ketenes to Acetylenic Ethers

View PDF

Table XVI. [2 + 2] Cycloaddition of Ketenes to Ynamines

View PDF

Table XVII. [2 + 2] Cycloaddition of Ketenes to Organometallic Acetylenes

View PDF

Table XVIII. [2 + 2] Cycloaddition of Ketenes to Aldehydes

View PDF

Table XIX. [2 + 2] Cycloaddition of Ketenes to Ketones

View PDF

Table XX. [2 + 2] Cycloaddition of Ketenes to Thiocarbonyl Compounds

View PDF

Table XXI. Olefins from Reaction of Ketenes with Carbonyl and Thiocarbonyl Compounds

View PDF

Table XXII. [2 + 2] Cycloaddition of Ketenes to Isocyanates

View PDF

Table XXIII. [2 + 2] Cycloaddition of Ketenes to Carbodiimides

View PDF

Table XXIV. [2 + 2] Cycloaddition of Ketenes to *N*-Sulfinylamines

View PDF

Table XXV. [2 + 2] Cycloaddition of Ketenes to Nitroso Compounds

View PDF

Table XXVI. [2 + 2] Cycloaddition of Ketenes to Azo Compounds

View PDF

Table XXVII. [3 + 2] Cycloadditions

View PDF

Table XXVIII. [4 + 2] Cycloaddition of Ketenes to Dienes

View PDF

Table XXIX. [4 + 2] Cycloaddition of Ketenes to Azadienes

View PDF

Table XXX. [4 + 2] Cycloaddition of Ketenes to Amidines

View PDF

Table XXXI. [4 + 2] Cycloaddition of Ketenes to *o*-Quinones and Quinonimines

View PDF

Table XXXII. [4 + 2] Cycloaddition of Ketenes to α , β-Unsaturated Carbonyl Compounds

View PDF

Table XXXIII. [4 + 2] Cycloaddition of Ketenes to α , β -Unsaturated Thiocarbonyl Compounds

View PDF

Table XXXIV. [4 + 2] Cycloaddition of Ketenes to Isocyanates and Isothiocyanates

View PDF

Table XXXV. [4 + 2] Cycloaddition of Ketenes to Azo Compounds

View PDF

Table XXXVI. [4 + 2] Cycloaddition of Ketenes to Thioacyl Imines

View PDF

Table XXXVII. [4 + 2] Cycloaddition of Ketenes to Mesoionic Compounds

View PDF

Table XXXVIII. [4 + 2] Cycloaddition of Acyl and Vinyl Ketenes to Olefins

View PDF

Table XXXIX. [4 + 2] Cycloaddition of Acyl and Vinyl Ketenes to Acetylenes

View PDF

Table XL. [4 + 2] Cycloaddition of Acyl and Vinyl Ketenes to Aldehydes

View PDF

Table XLI. [4 + 2] Cycloaddition of Acyl Ketenes to Ketones

View PDF

Table XLII. [4 + 2] Cycloaddition of Acyl and Vinyl Ketenes to Nitriles

View PDF

Table XLIII. [4 + 2] Cycloaddition of Acyl Ketenes to Cyanates

View PDF

Table XLIV. [4 + 2] Cycloaddition of Acyl Ketenes to Isocyanates and Isothiocyanates

View PDF

Table XLV. [4 + 2] Cycloaddition of Acyl Ketenes to *N*-Sulfinylamines

View PDF

Table XLVI. [4 + 2] Cycloaddition of Acyl Ketenes to Carbodiimides

View PDF

Table XLVII. [4 + 2] Cycloaddition of Acyl and Vinylketenes to Imines and Azo Compounds

View PDF

TABLE I. KETENE DIMERS

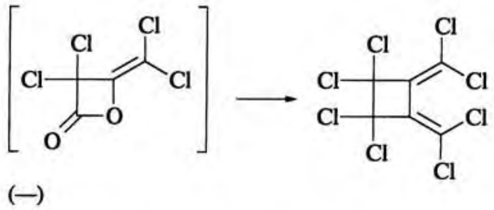
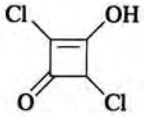
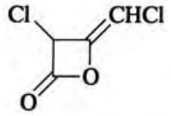
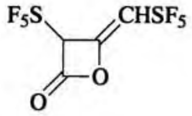
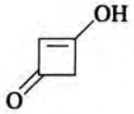
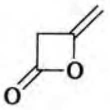
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
$Cl_2CHCOBr$	Zn, Et_2O or octane	(—)	7
$Cl_2CHCOCl$	Et_3N, n-C_6H_{14}, acenaphthalene	 (—)	63
$BrCH_2COBr$	Et_3N, Et_2O, -78°	(—)	328
$ClCH_2COCl$	Et_3N, Et_2O	 +  (—)	329
$ClCH_2COBr$	Et_3N, Et_2O, -78°	(—)	328
FCH_2COCl	Et_3N, Et_2O, -78°	(—)	328
$F_5SCH_2CO_2H$	P_4O_{10}, 60-160°	 (—)	330
$CH_2=C=O$	(—)	 (4-5) +  (88-90)	59

TABLE I. KETENE DIMERS (*Continued*)

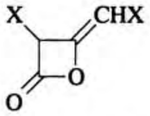
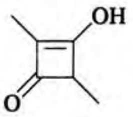
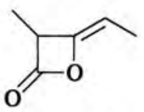
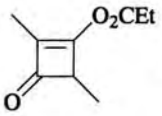
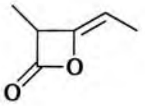
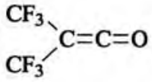
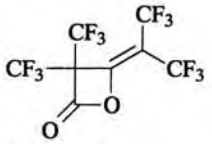
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
XCH_2COX	Et_3N, Et_2O	 X = Br (40) X = Cl (50)	331
C_3			
MeCHBrCOBr	Zn, $ZnCl_2$, Et_2O, -5°	 (5)	332, 333
	Zn, THF, -30°	" (88)	334
EtCOCl	Et_3N, Et_2O	 (74)	331
$(EtCO)_2O$	Pyrolysis	 (76) +  (13)	335
C_4			
 $(CF_3)_2C=C=O$	—	(—)	65, 336
	Et_2NO	 (60)	66
	Et_3NF	" (91)	65

TABLE I. KETENE DIMERS (*Continued*)

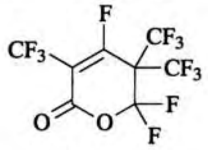
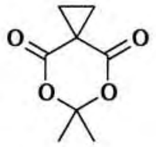
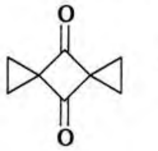
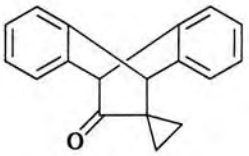
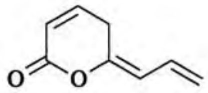
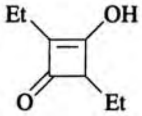
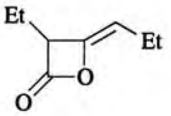
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N	 (79)	67
	500°, 0.05 mm	 (45)	304
	*hν* (Corex), pentane	" (38)	309
$CH_2=CHCH=C=O$	rt	 (70)	337
EtCHBrCOBr	Zn, THF, -50°	 (19)	334, 332
n-PrCOCl	Et_3N, ligroin	 (70)	331, 338

TABLE I. KETENE DIMERS (*Continued*)

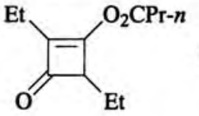
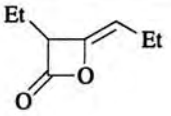
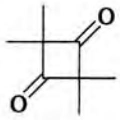
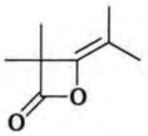
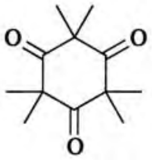
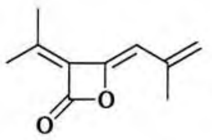
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$(n\text{-}PrCO)_2O$	Pyrolysis	 (40) +  (10)	335
$Me_2CHCOCl$	Et_3N, CS_2	 I (18)	339
$Me_2C=C=O$	Various solvents	I (99)	40, 340, 341
	$P(OEt)_3$	I (4) +  (93)	342
	$AlCl_3$, PhMe, -56°	 (54)	62
C_5			
$Me_2C=CHCOCl$	Me_3N, hexane	 (60)	343

TABLE I. KETENE DIMERS (*Continued*)

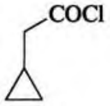
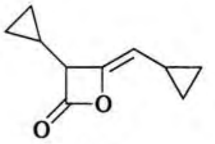
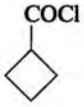
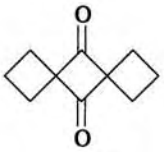
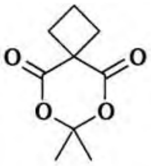
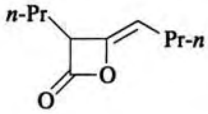
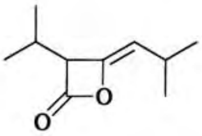
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N	 (—)	344
	Et_3N, C_6H_6, Et_2O	 (70)	345
	430°, 0.003 mm	" (100)	304
n-BuCOCl	Et_3N, ligroin	 (93)	331
i-BuCOCl	Et_3N, Et_2O	 **I** (56)	331

TABLE I. KETENE DIMERS (*Continued*)

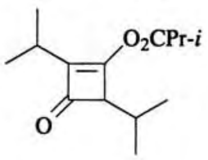
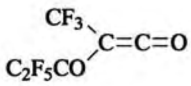
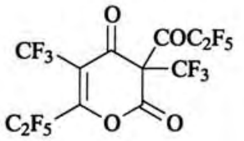
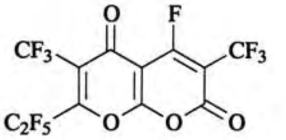
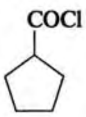
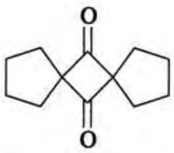
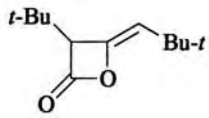
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
(*i*-PrCO)$_2$O	Pyrolysis	**I** (9) +  (57)	335
C_6			
 $(CF_3)(C_2F_5CO)C{=}C{=}O$	CsF (cat.), tetraglyme	 (90)	346
	CsF (molar), tetraglyme	 (47)	346
	Et_3N, Et_2O	 (85)	345
t-BuCH$_2$COCl	Et_3N	 (30)	347

TABLE I. KETENE DIMERS (*Continued*)

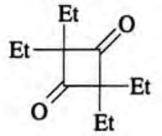
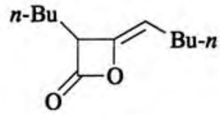
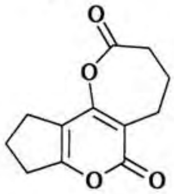
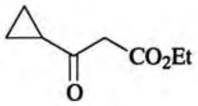
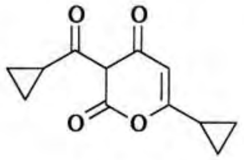
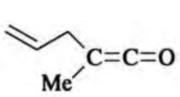
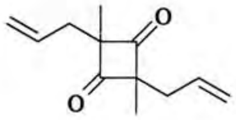
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$Et_2C=C=O$	25°, 48 d	 (83)	341, 348
n-$C_5H_{11}COCl$	Et_3N, ligroin	 (40)	331
$ClOC(CH_2)_4COCl$	Et_3N, Et_2O	 (4)	349
	410°	 (79)	350
	30°, 4 d	 (78)	341

TABLE I. KETENE DIMERS (*Continued*)

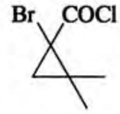
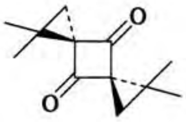
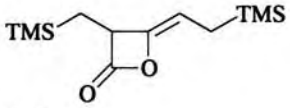
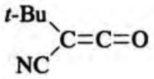
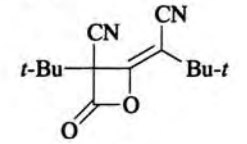
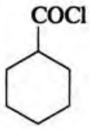
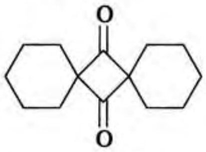
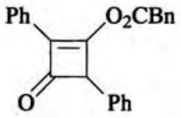
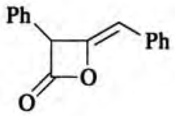
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$ZnCl_2$	 (45)	351
$TMS(CH_2)_2COCl$	Et_3N, hexane	 (85)	352
	C_6H_6	(—)	353, 68
C_7 	Et_3N, C_6H_6	 (—)	68
	Et_3N, Et_2O	 (82)	345, 354, 355
C_8 BnCOCl	Et_3N, Et_2O	 (67)	356, 71
PhCHClCOCl	Zn, Et_2O	 (14)	357

TABLE I. KETENE DIMERS (*Continued*)

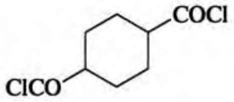
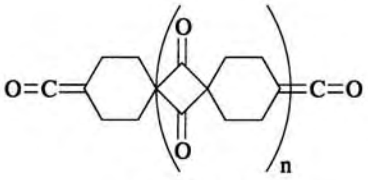
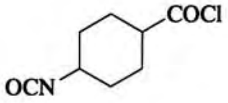
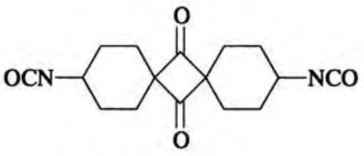
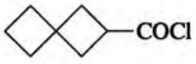
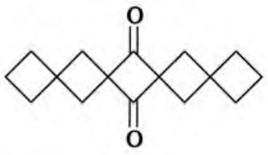
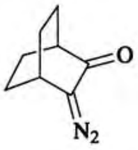
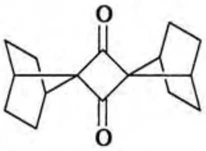
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	Et_3N, C_6H_6	 n = 1, 2, 3, 4	(—)	358
	PhNHMe, dioxane, 80°		(74)	359
	Et_3N, C_6H_6		(77)	360
	Cu, C_6H_6		(46)	313

TABLE I. KETENE DIMERS (*Continued*)

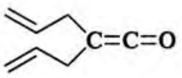
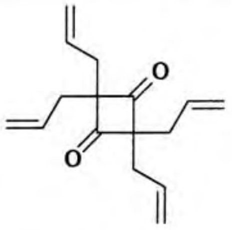
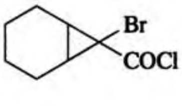
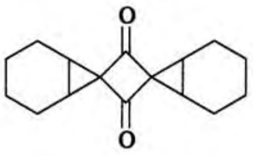
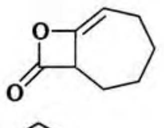
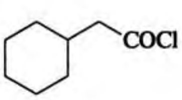
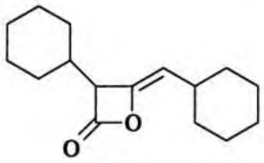
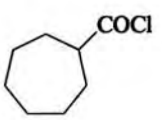
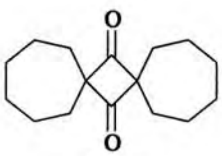
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	30°, 11 d		(—)	341
	Zn-Ag		(20)	351
$ClOC(CH_2)_6COCl$	Et_3N, Et_2O		(—)	361
	Et_3N		(40)	355
	Et_3N, C_6H_6		(8)	362

TABLE I. KETENE DIMERS (*Continued*)

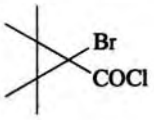
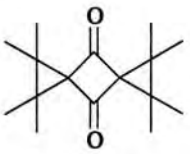
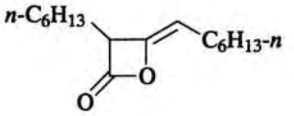
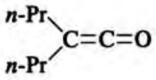
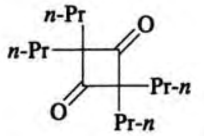
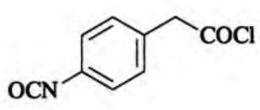
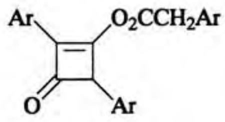
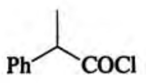
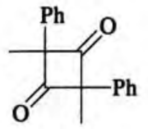
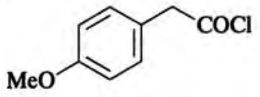
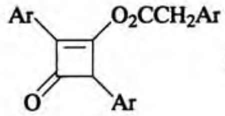
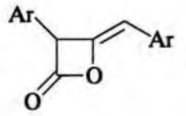
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Zn-Ag	 (45)	351
n-$C_7H_{15}COCl$	Et_3N, Et_2O	 (56)	331
 $(n\text{-Pr})_2C=C=O$	25°, 77 d	 (10)	341
	Et_3N, Et_2O	 (35)	359
	Et_3N, 100°	 *cis*, (10) *trans*, (46)	363
C_9 	Et_3N	 (40) +  (5)	71, 364

TABLE I. KETENE DIMERS (*Continued*)

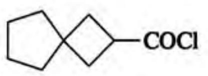
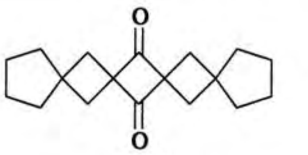
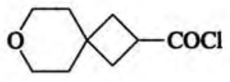
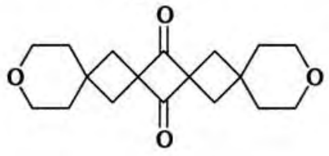
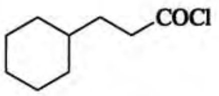
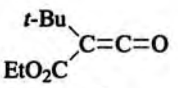
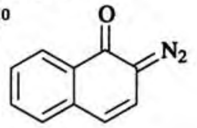
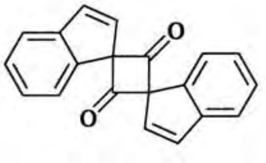
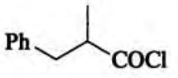
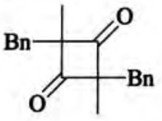
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N, C_6H_6	 (42)	360
	Et_3N, C_6H_6	 (54)	365
	Et_3N	Liquid dimer (18)	355
 $(t\text{-Bu})(EtO_2C)C=C=O$	rt, 2 min	No dimerization	69
C_{10} 	Xylene, reflux	 (—)	366
	Et_3N, 100°	 (19) *trans:cis* = 40:60	363

TABLE I. KETENE DIMERS (*Continued*)

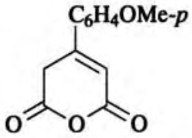
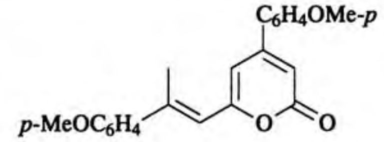
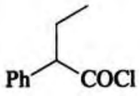
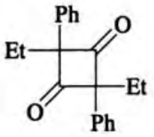
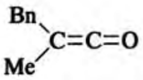
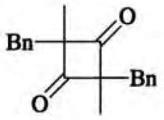
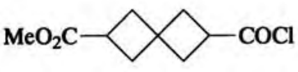
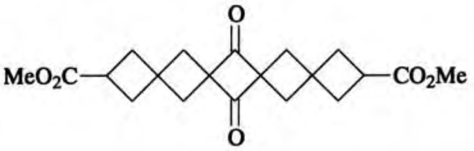
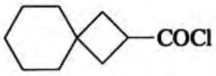
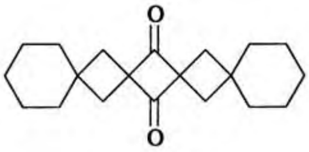
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PhCO_2Na$, $PhCO_2H$, 140-150°	 (26)	367
	Et_3N, 100°	 (28) *trans:cis* = 38:62	363
 $\mathrm{Bn(Me)C{=}C{=}O}$	Et_3N, 100°	 (—)	341
	Et_3N, 100°	 (50)	368
	Et_3N, C_6H_6	 (65)	360

TABLE I. KETENE DIMERS (*Continued*)

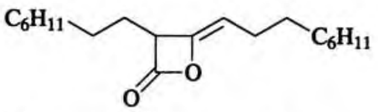
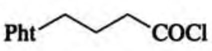
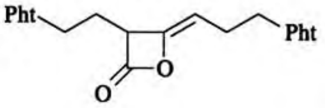
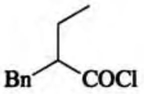
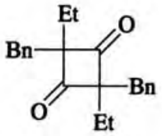
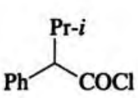
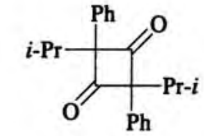
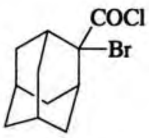
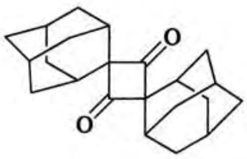
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N	 (25)	355
C_{11}			
	Et_3N	 (—)	369
	Et_3N, 100°	 (14) *trans:cis* = 42:58	363
	Me_3N, 100°	 (9)	363
	Zn, Et_2O	 (79)	370

TABLE I. KETENE DIMERS (*Continued*)

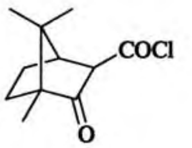
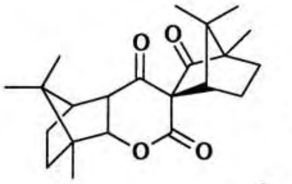
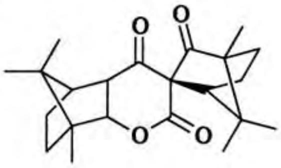
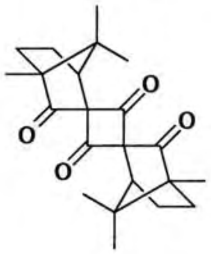
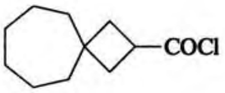
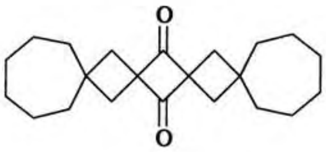
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N, Et_2O	 (87)	371
		+  (—)	
	Quinoline , Et_2O	 (—)	372
	Et_3N, C_6H_6	 (50)	362

TABLE I. KETENE DIMERS (*Continued*)

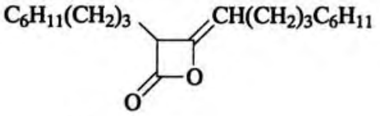
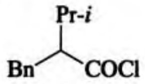
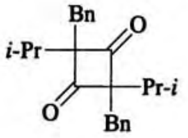
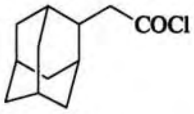
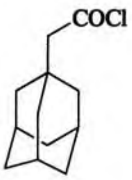
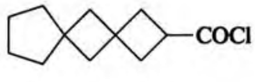
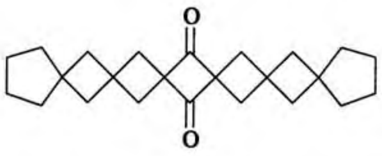
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6H_{11}(CH_2)_4COCl$	Et_3N	 (36)	355
C_{12}			
	Et_3N, 100°	 (3) *trans:cis* = 36:64	363
	Et_3N, Et_2O	—	370
	Et_3N, Et_2O	—	370
	Et_3N, C_6H_6	 (61)	360

TABLE I. KETENE DIMERS (*Continued*)

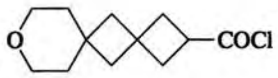
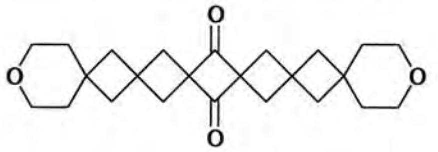
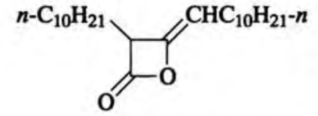
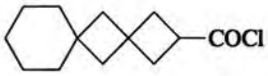
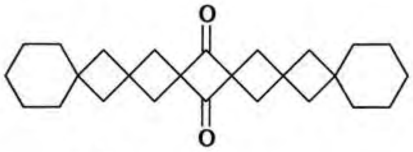
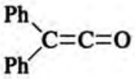
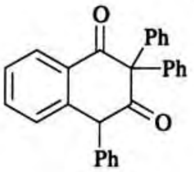
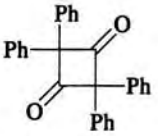
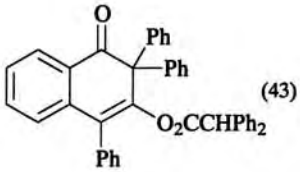
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N, C_6H_6	 (50)	365
n-$C_{11}H_{23}COCl$	Et_3N, Et_2O	 (100)	331
C_{13}			
	Et_3N, C_6H_6	 (38)	360
C_{14}			
 $Ph_2C=C=O$	PhCOCl, 100°	 (—)	61
	200°, 6 h	 (8) +  (43)	61, 373

TABLE I. KETENE DIMERS (*Continued*)

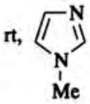
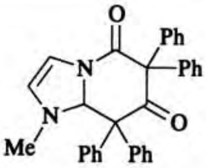
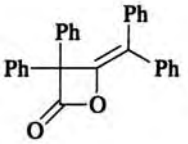
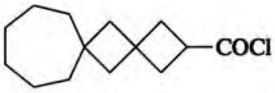
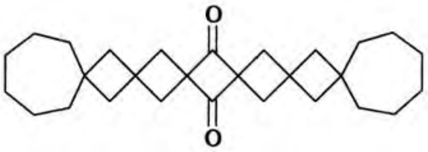
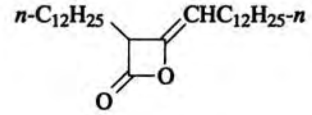
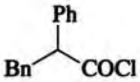
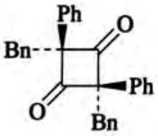
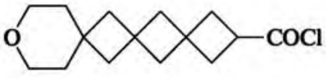
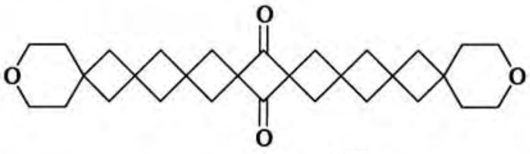
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	rt, 	 +  (6-30)	374, 375
	Et_3N, C_6H_6	 (55)	362
n-$C_{13}H_{27}COCl$	Et_3N, ligroin	 (—)	331
 $PhCH(Bn)COCl$	Et_3N, 100°	 (18)	376
	Et_3N, C_6H_6	 (18)	365

TABLE I. KETENE DIMERS (*Continued*)

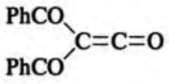
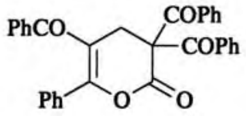
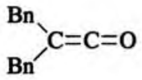
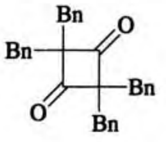
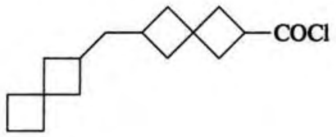
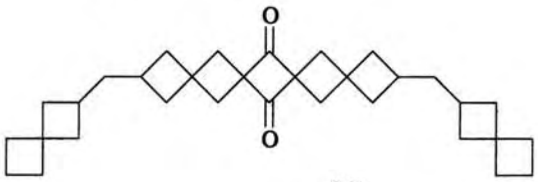
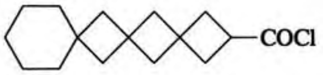
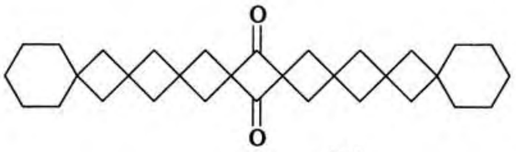
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	> -75°		(—)	377
C_{16}				
	25°, 24 h		(—)	341, 378
	Et_3N, C_6H_6		(20)	360
	Et_3N, C_6H_6		(53)	360

TABLE I. KETENE DIMERS (*Continued*)

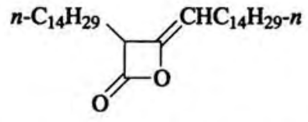
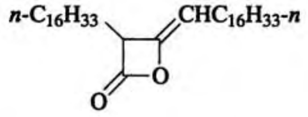
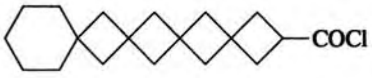
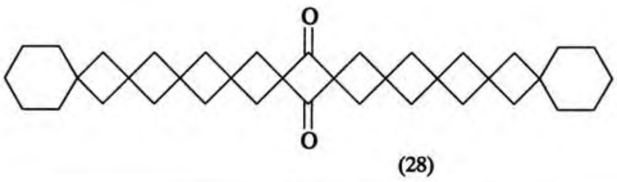
Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
n-$C_{15}H_{31}COCl$	Et_3N, Et_2O		(very high)	379
C_{18}				
n-$C_{17}H_{35}COCl$	Et_3N, C_6H_6		(90)	331
	Et_3N, C_6H_6		(28)	360

TABLE II. MIXED KETENE DIMERS

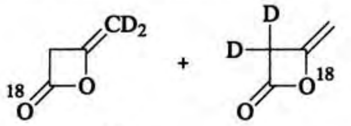
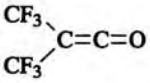
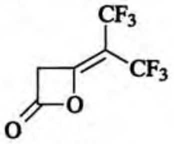
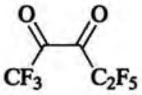
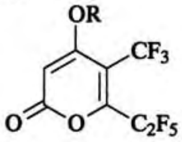
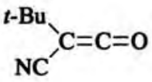
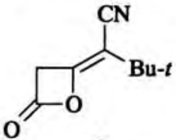
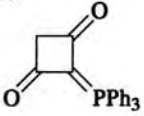
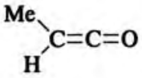
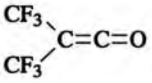
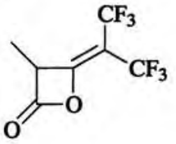
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
$CD_2=C=O$	$CH_2=C=O^{18}$	0°	 (—)	380
$CH_2=C=O$	 $(CF_3)_2C=C=O$	-78°	 (89)	336
		Et_2O, -20°	 R = H, Ac (67)	346
	 $t\text{-Bu}(NC)C=C=O$	PhMe	 (36)	43
	$Ph_3P=C=C=O$	C_6H_6, rt	 (—)	381
C_3				
 $Me(H)C=C=O$	 $(CF_3)_2C=C=O$	-80°	 (61)	336

TABLE II. MIXED KETENE DIMERS (*Continued*)

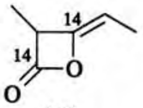
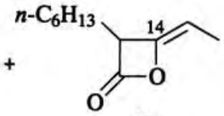
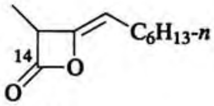
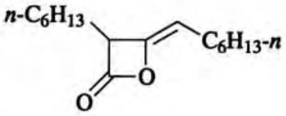
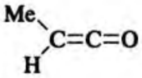
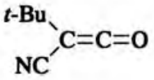
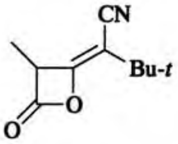
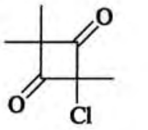
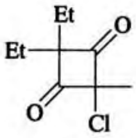
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$Et^{14}COCl$	$n\text{-}C_7H_{15}COCl$	Et_3N, Et_2O, rt	 (25) +  (8) +  (17) +  (24)	382
 $Me(H)C=C=O$	 $t\text{-Bu}(NC)C=C=O$	PhMe	 (49)	41,43
MeCHClCOCl	$Me_2CHCOCl$	Et_3N, C_6H_6	 (34)	73
	$Et_2CHCOCl$	Et_3N, C_6H_6, reflux 4 d	 (63)	383, 73

TABLE II. MIXED KETENE DIMERS (*Continued*)

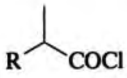
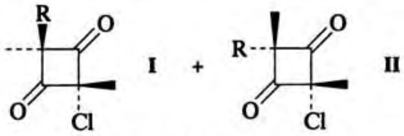
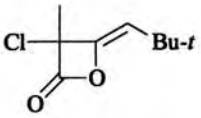
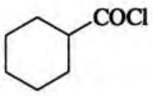
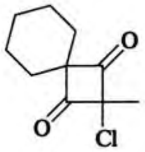
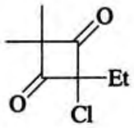
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, C_6H_6	 R — I + II — I:II *n*-Pr — (42) — 1:1 *i*-Pr — (57) — 1:1	347
	t-$BuCH_2COCl$	Et_3N, C_6H_6	 (32)	347
		Et_3N, C_6H_6	 (62)	73, 383
C_4				
$Me_2CHCOCl$	EtCHClCOCl	Et_3N, C_6H_6	 (41)	73

TABLE II. MIXED KETENE DIMERS (*Continued*)

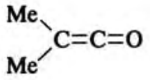
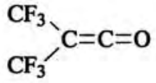
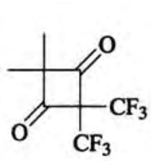
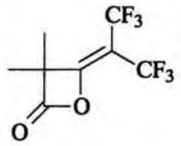
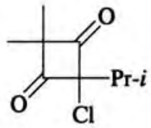
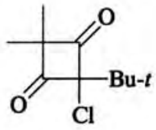
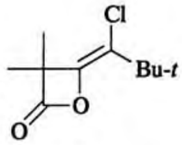
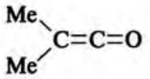
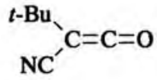
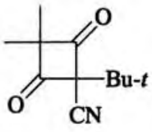
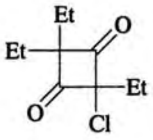
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
 $Me_2C{=}C{=}O$	 $(CF_3)_2C{=}C{=}O$		 + 	336
		Cyclohexane	(81) (0)	
		EtOAc	(19) (24)	
$Me_2CHCOCl$	*i*-PrCHClCOCl	Et_3N, C_6H_6, rt	 (40)	73
	t-BuCHClCOCl	Et_3N, C_6H_6	 +  (56) (13)	73
 $Me_2C{=}C{=}O$	 $t\text{-}Bu(NC)C{=}C{=}O$	PhMe	 (38)	43,41
EtCHClCOCl	$Et_2CHCOCl$	Et_3N, C_6H_6	 (65)	383, 73

TABLE II. MIXED KETENE DIMERS (*Continued*)

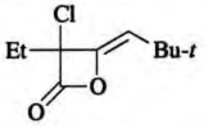
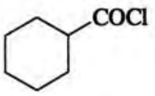
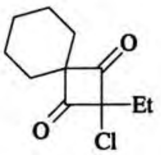
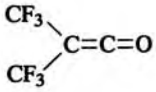
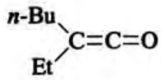
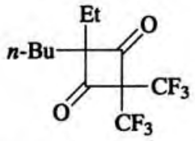
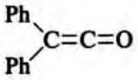
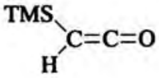
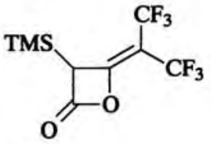
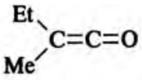
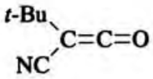
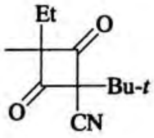
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	t-BuCH$_2$COCl	Et$_3$N, C$_6$H$_6$	 (10)	347
		Et$_3$N, C$_6$H$_6$	 (35)	73
 $(CF_3)_2C{=}C{=}O$	 $n\text{-}Bu(Et)C{=}C{=}O$	Hexane	 (—)	336
	 $Ph_2C{=}C{=}O$	100°, 1 week	(—)	336
	 $TMS(H)C{=}C{=}O$	-78°	 (—)	384
C$_5$				
 $Et(Me)C{=}C{=}O$	 $t\text{-}Bu(NC)C{=}C{=}O$	PhMe	 (44)	43

TABLE II. MIXED KETENE DIMERS (*Continued*)

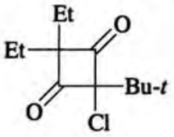
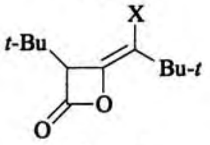
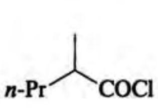
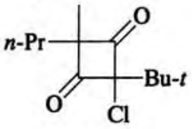
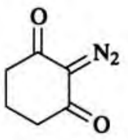
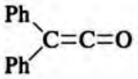
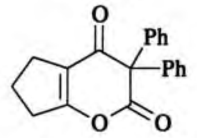
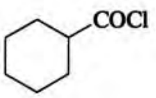
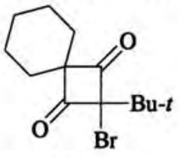
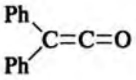
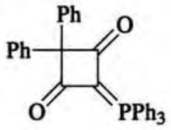
Ketene or Ketene Source	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_6$				
Et$_2$CHCOCl	t-BuCHClCOCl	Et$_3$N, C$_6$H$_6$	 (43)	73
t-BuCH$_2$COCl	t-BuCHXCOCl	Et$_3$N, C$_6$H$_6$	 X = Cl (20) X = Br (10)	347
	t-BuCHClCOCl	Et$_3$N, C$_6$H$_6$	 (48)	347
	 $Ph_2C{=}C{=}O$	Xylene, 140°	 (—)	385
t-BuCHBrCOCl		Et$_3$N, C$_6$H$_6$	 (36)	73
 $Ph_2C{=}C{=}O$	Ph$_3$P=C=C=O	C$_6$H$_6$, rt	 (—)	381

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS

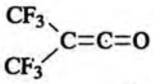
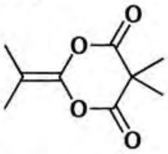
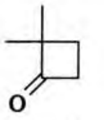
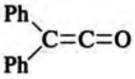
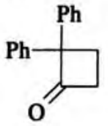
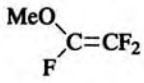
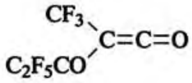
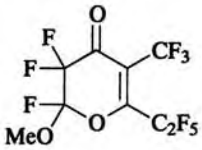
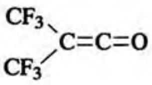
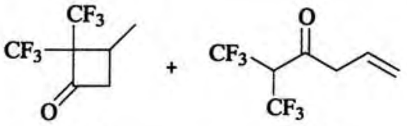
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
$CH_2{=}CH_2$	 $(CF_3)_2C{=}C{=}O$	130-200°	(—)	84
		140°	 (60)	316
	 $Ph_2C{=}C{=}O$	85-90°, 12 d	 (60)	386
C_3				
 $MeO(F)C{=}CF_2$	 $CF_3(C_2F_5CO)C{=}C{=}O$	100°	 (73)	346
$MeCH{=}CH_2$	 $(CF_3)_2C{=}C{=}O$	150°, 8 h	 I II I + II (19); I:II = 2.3	84

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

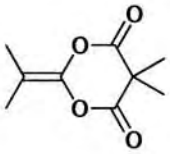
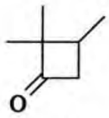
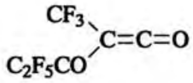
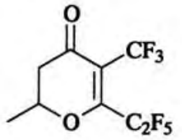
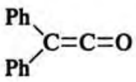
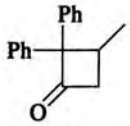
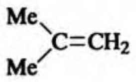
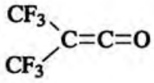
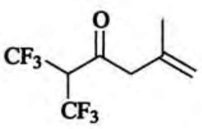
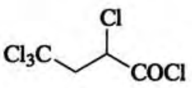
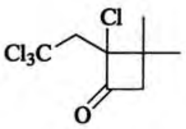
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		K_2CO_3 (cat.), PhMe, 130°	 (72)	316
	 $CF_3(C_2F_5CO)C{=}C{=}O$	150°, 8 h	 (20)	346
	 $Ph_2C{=}C{=}O$			386
		C_6H_6, 110-115°, 2 d	(43)	
		rt, 8 min	(97)	
C_4				
 $Me_2C{=}CH_2$	 $(CF_3)_2C{=}C{=}O$	100°	 (86)	84, 387
	 $Cl_3CCH_2CH(Cl)COCl$	Et_3N, cyclohexane	 (67)	388, 389

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

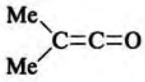
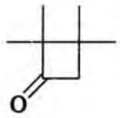
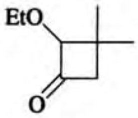
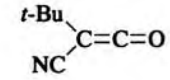
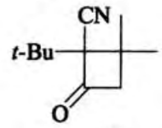
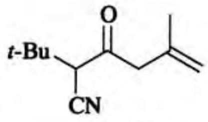
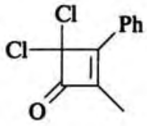
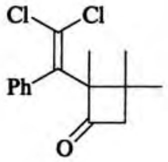
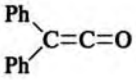
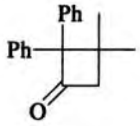
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C=C=O$	140°	 (65)	390, 37
	$EtOCH_2COCl$	Et_3N	 (30)	391
	 $t\text{-Bu}(NC)C=C=O$	C_6H_6, 78°	 +  (44) (22)	392
		*h*ν, C_6H_6	 (40)	306
	 $Ph_2C=C=O$	70°, 8 d	 (66)	386

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

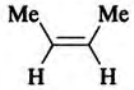
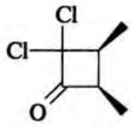
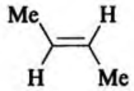
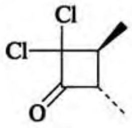
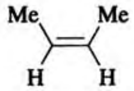
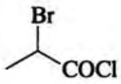
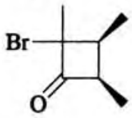
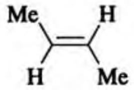
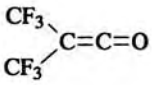
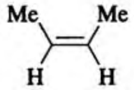
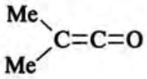
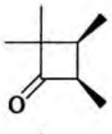
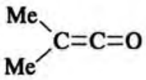
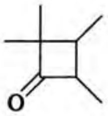
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, $POCl_3$, Et_2O	 (79)	82
	Cl_3CCOCl	Zn, $POCl_3$, Et_2O	 (80)	82
		Et_3N, hexane	 (22)	393
	 $(CF_3)_2C=C=O$	100°, overnight	(—)	84
	 $Me_2C=C=O$	100°	 (—)	37
	 $Me_2C=C=O$	C_6H_6, 105°, 8 h	 **I** (94) *cis:trans* = 97.5:2.5	294

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

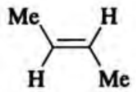
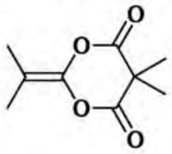
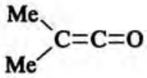
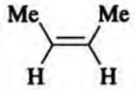
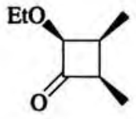
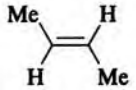
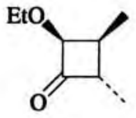
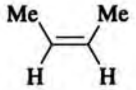
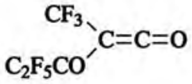
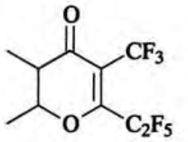
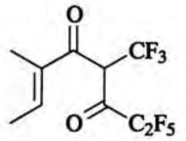
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 105°, 3 h, K_2CO_3	I (70) *cis:trans* = 95:5	294
	"	C_6H_6, 105°, 8 h	I (10) *cis:trans* = 40:60	294
	"	C_6H_6, 105°, 3 h, K_2CO_3	I (32) *cis:trans* = 19:81	294
	 $Me_2C{=}C{=}O$	100°	I (—)	37
	$EtOCH_2COCl$	Et_3N	 (45)	391
	$EtOCH_2COCl$	Et_3N	 (31)	391
		95°, 310 h	 (10) +  (1)	346

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

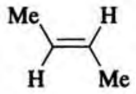
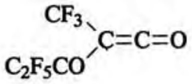
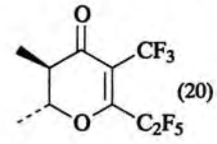
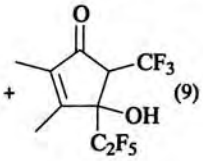
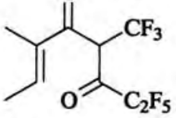
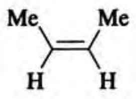
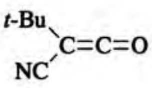
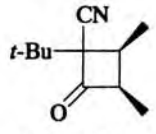
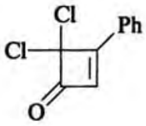
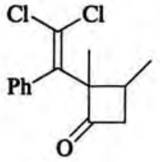
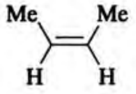
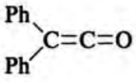
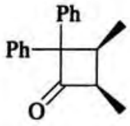
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		95°, 310 h	 (20) +  (9) +  (10)	346
		C_6H_6, 78°	 (—)	394
MeCH=CHMe		*hv*, C_6H_6	 (30)	306
		90-95°, 3 d	 (96)	386, 395

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

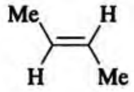
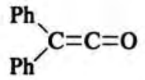
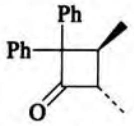
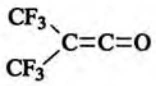
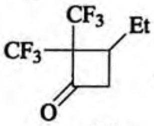
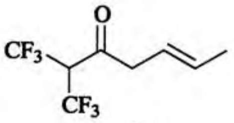
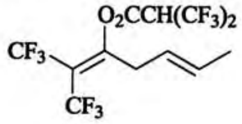
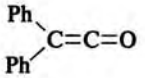
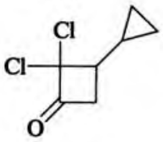
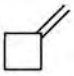
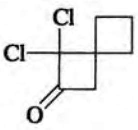
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	90-95°, 3 min	 (46)	386, 395
$EtCH{=}CH_2$	 $(CF_3)_2C{=}C{=}O$	100°, 37 d	 (10) +  (17) +  (34)	84
$MeSCH_2CH{=}CH_2$	Cl_3CCOCl	Zn, $MeCH(OMe)_2$, reflux 60 h	(—)	299
C_5 	 $Ph_2C{=}C{=}O$	98°, 2 weeks	(—)	396
	Cl_3CCOCl	Zn, Et_2O	 (58)	78
	Cl_3CCOCl	Zn, Et_2O	 (60)	397, 398

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

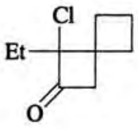
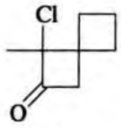
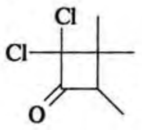
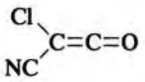
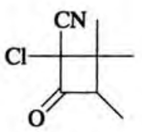
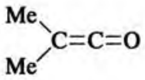
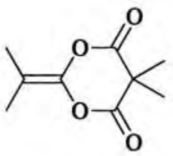
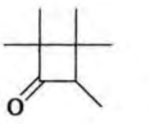
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtCHClCOCl	Et_3N, C_6H_{14}	 (35)	399
	MeCHClCOCl	Et_3N, C_6H_{14}	 (30)	399
$Me_2C{=}CHMe$	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	 (87)	82, 317
	Cl_3CCOCl	Zn, Et_2O	" (73)	400
	 $Cl(NC)C{=}C{=}O$	PhMe, 110°, 1.75 h	 (80)	312
	 $Me_2C{=}C{=}O$	100°	(—)	37
		PhMe, 110°, K_2CO_3	 (30)	293

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

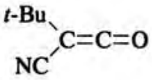
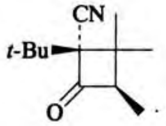
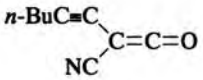
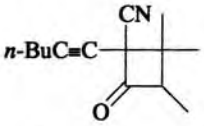
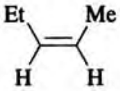
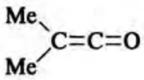
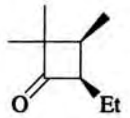
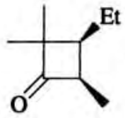
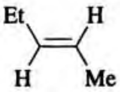
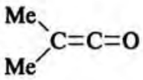
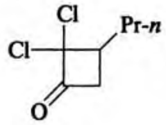
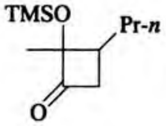
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 5°	 (86)	401
		C_6H_6, 80°	 (45)	402
		100°	 I +  II (—) I:II = 51:49	37
		100°	(—)	37
n-PrCH=CH_2	Cl_3CCOCl	Zn, Et_2O	 (58)	400, 403
	MeCOCOTMS	$h\nu$, C_5H_{10}	 (—)	307

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

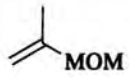
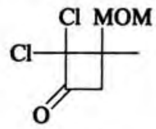
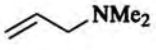
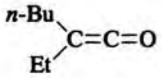
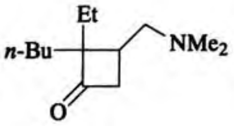
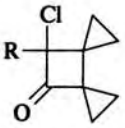
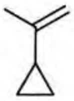
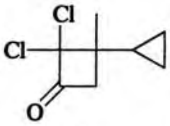
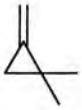
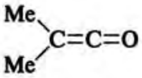
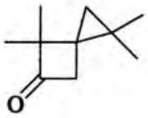
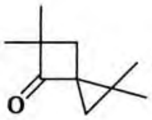
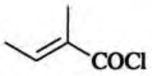
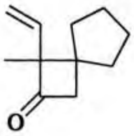
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O	 (56)	404, 299
		180°	 (32)	405
C_6				
	$Cl_2RCCOCl$	Zn, Et_2O	 R = H (63) R = Cl (59)	406, 407
	Cl_3CCOCl	Zn, Et_2O	 (56-60)	78
		120°	 (36) +  (29)	408
		Et_3N	 (79)	409

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

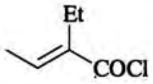
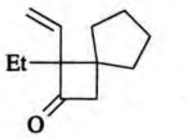
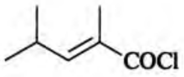
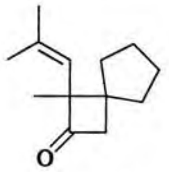
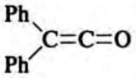
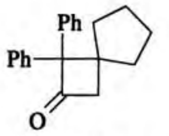
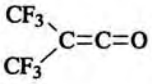
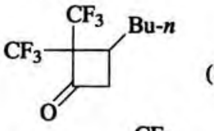
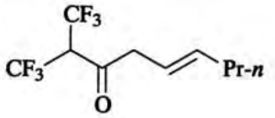
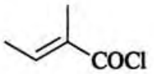
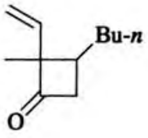
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 (67)	409
		Et_3N	 (20)	409
	 $Ph_2C=C=O$	100°	 (—)	410
n-BuCH=CH_2	 $(CF_3)_2C=C=O$	150°, 8 h	 (12) +  (8)	84
		Et_3N, $CHCl_3$	 (24)	411

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

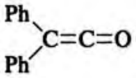
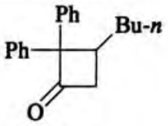
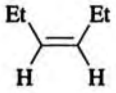
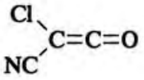
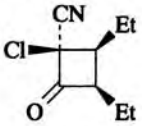
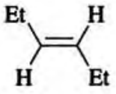
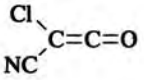
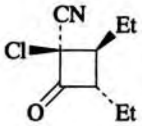
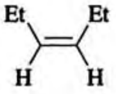
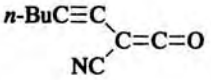
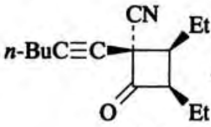
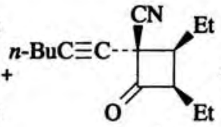
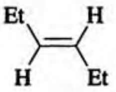
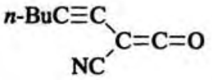
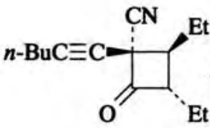
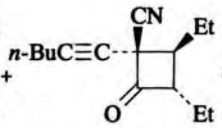
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	100°	 (87-91)	386
	 $Cl(NC)C=C=O$	PhMe, 103°, 1.75 h	 (93)	312
	 $Cl(NC)C=C=O$	PhMe, 103°, 1.75 h	 (67)	312
	 $n\text{-}BuC{\equiv}C(NC)C=C=O$	C_6H_6, 80°	 (48) +  (12)	402
	 $n\text{-}BuC{\equiv}C(NC)C=C=O$	C_6H_6, 80°	 (38) +  (38)	402

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

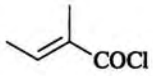
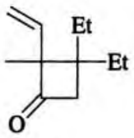
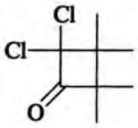
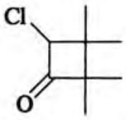
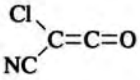
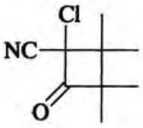
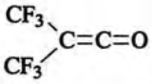
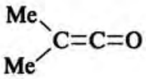
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$CH_2{=}CEt_2$		Et_3N	 (12)	409
$Me_2C{=}CMe_2$	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	 (61)	82, 298
	Cl_3CCOCl	Zn, Et_2O	" (75)	400
	$Cl_2CHCOCl$	Zn, Et_2O	 (55)	400
	 $\mathrm{(Cl)(NC)C{=}C{=}O}$	PhMe, 103°, 1.75 h	 (74)	312
	 $\mathrm{(CF_3)_2C{=}C{=}O}$	100°, 45 d	(—)	84
	 $\mathrm{Me_2C{=}C{=}O}$	100°	(—)	37

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

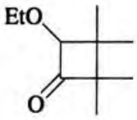
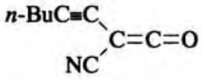
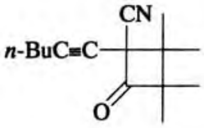
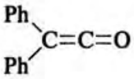
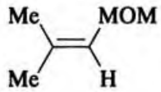
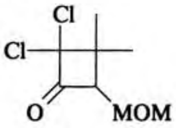
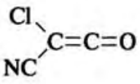
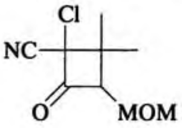
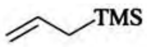
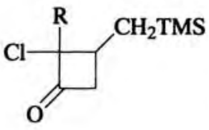
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$EtOCH_2COCl$	Et_3N	 (43)	391
	 $\mathrm{(\mathit{n}\text{-}BuC{\equiv}C)(NC)C{=}C{=}O}$	C_6H_6, 80°	 (50)	402
	 $\mathrm{Ph_2C{=}C{=}O}$	(—)	(—)	412
	Cl_3CCOCl	Zn, $MeCH(OMe)_2$, reflux 40-60 h	 (76)	299, 404
	 $\mathrm{(Cl)(NC)C{=}C{=}O}$	PhMe	 (15)	404
	$RClHCCOCl$	Et_3N, C_6H_{14}	 R = Cl (54) R = Me (62)	352

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

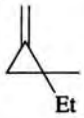
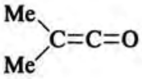
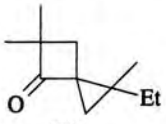
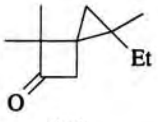
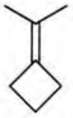
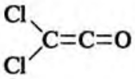
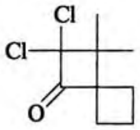
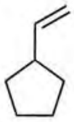
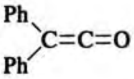
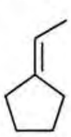
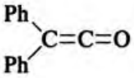
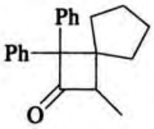
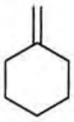
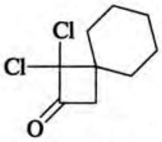
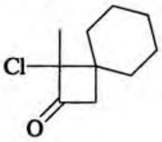
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	 $Me_2C=C=O$	120°	 (29) +  (36)	408
	 $Cl_2C=C=O$	—	 (—)	413
	 $Ph_2C=C=O$	100°	(—)	410
	 $Ph_2C=C=O$	100°, 12 h	 (—)	410
	$Cl_2CHCOCl$	Et_3N	 (55)	414, 415
	MeCHClCOCl	Et_3N, C_6H_{14}	 (60)	399, 416

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

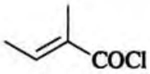
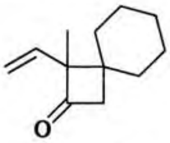
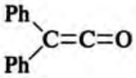
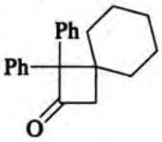
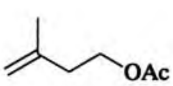
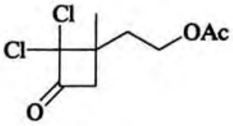
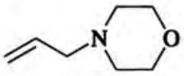
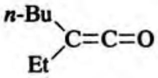
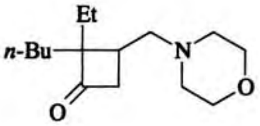
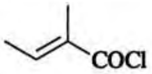
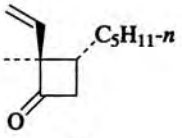
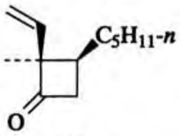
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 (42)	409
	 $Ph_2C=C=O$	100°	 (—)	410
	Cl_3CCOCl	Zn-Cu, Et_2O	 (68)	417
	 $n\text{-}Bu(Et)C=C=O$	180°, 8 h	 (28)	405
$n\text{-}C_5H_{11}CH=CH_2$		Et_3N	 (28) +  (12)	409

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

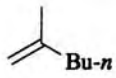
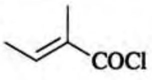
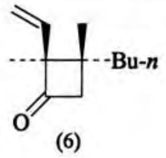
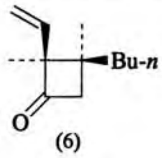
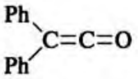
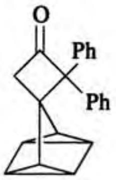
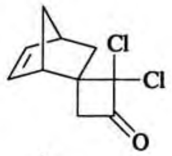
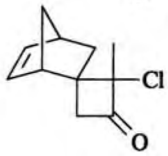
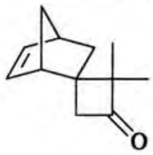
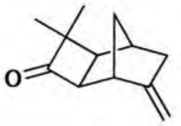
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 (6) +  (6)	409
C_8				
	 $Ph_2C=C=O$	70°, 6 h	 (80)	418
	Cl_3CCOCl	Zn, Et_2O	 (60)	400
	MeCHClCOCl	Et_3N, C_6H_{14}	 (65)	399
	$Me_2CHCOCl$	Et_3N, C_6H_{14}	 +  (10)	399

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

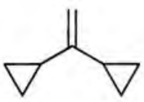
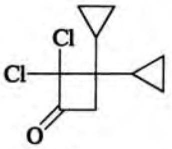
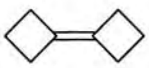
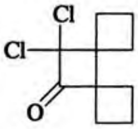
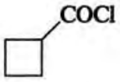
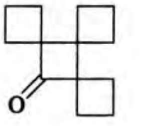
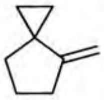
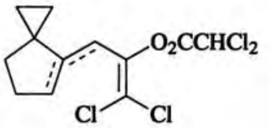
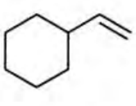
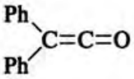
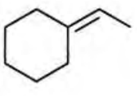
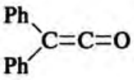
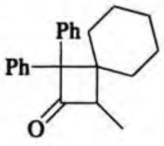
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O	 (56-60)	419
	Cl_3CCOCl	Zn-Cu	 (—)	420
		Et_3N	 (54)	421
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (30)	422
	 $Ph_2C=C=O$	100°	(—)	422
	 $Ph_2C=C=O$	100°	 (—)	410

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

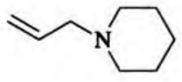
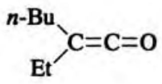
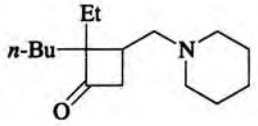
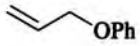
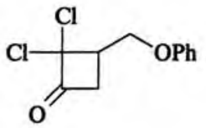
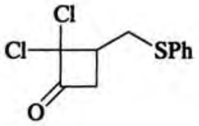
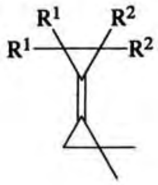
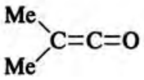
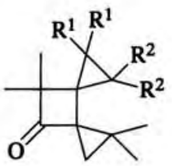
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $n\text{-Bu}(\text{Et})C{=}C{=}O$	180°	 (22)	405
C_9				
	Cl_3CCOCl	Zn, Et_2O	 (47)	404
	Cl_3CCOCl	$MeCH(OMe)_2$, Zn, reflux 40-60 h	" (86)	299
	Cl_3CCOCl	$MeCH(OMe)_2$, Zn, reflux 40-60 h	 (33)	299
C_{10}				
	 $Me_2C{=}C{=}O$	—	 R^1 = Me, R^2 = H (—) R^1 = H, R^2 = Me (—)	423

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

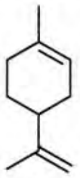
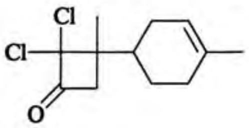
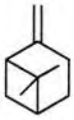
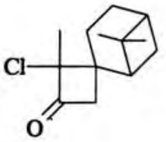
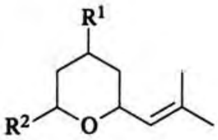
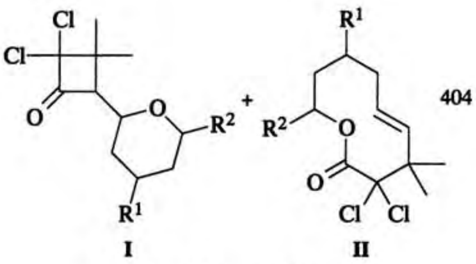
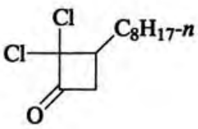
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O, ultrasound	 (80)	424
	$MeCHClCOCl$	Et_3N, C_6H_{14}	 (73)	416, 399
	Cl_3CCOCl	Zn, Et_2O	 R^1 R^2 I + II I:II Me H (76) 3:7 H Me (68) 15:85	404
$n\text{-}C_8H_{17}CH{=}CH_2$	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (88)	82,83

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

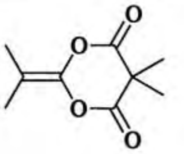
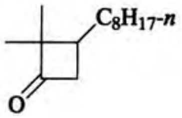
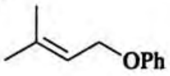
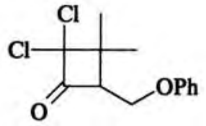
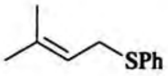
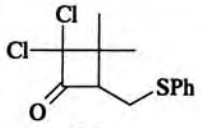
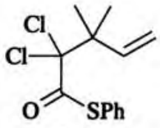
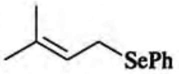
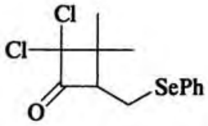
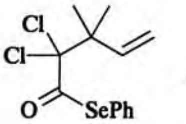
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 110°, K_2CO_3 (cat.)	 (67)	293
C_{11}				
	Cl_3CCOCl	Zn, $POCl_3$, glyme, reflux 40-60 h	 (65)	299
	Cl_3CCOCl	Zn, Et_2O	 I +  (19) (26)	404
	Cl_3CCOCl	Zn, $POCl_3$, glyme, reflux 40-60 h	" (66)	299
	Cl_3CCOCl	Zn, Et_2O	 + 	404

TABLE III. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC OLEFINS (*Continued*)

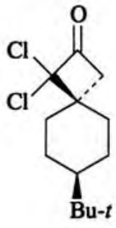
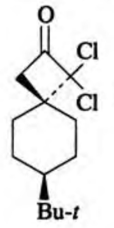
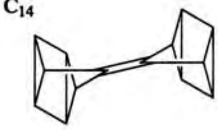
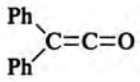
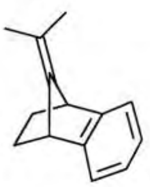
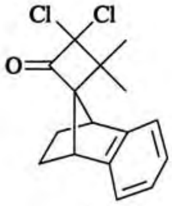
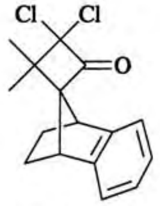
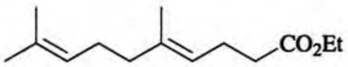
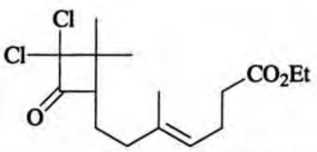
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 I +  II I + II (50), I:II = 4:1	414
C_{14}				
	 $Ph_2C=C=O$	—	(—)	425
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 +  (40) (13)	426
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (75)	75

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS

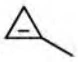
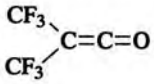
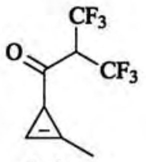
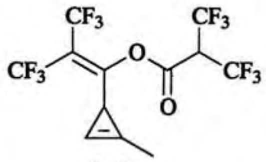
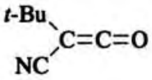
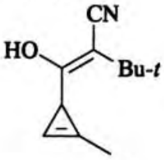
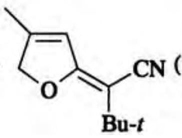
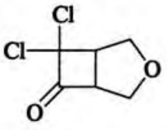
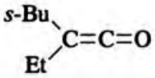
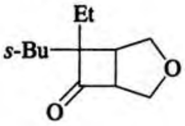
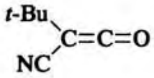
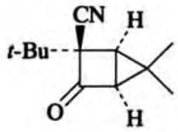
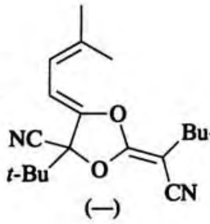
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 $(CF_3)_2C=C=O$	C_6H_6	 (—) +  (—)	79
	 $t\text{-Bu}(NC)C=C=O$	C_6H_6, 5°	 (73) +  (17)	79
	Cl_3CCOCl	Zn, Et_2O	 (40)	427, 404, 428
	 $s\text{-Bu}(Et)C=C=O$	180°	 (30)	321
C_5				
	 $t\text{-Bu}(NC)C=C=O$	25°, 5 h	 (—) +  (—)	429

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

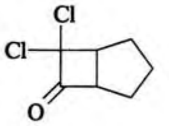
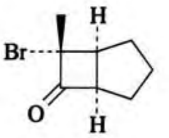
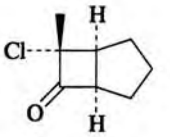
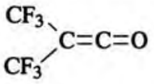
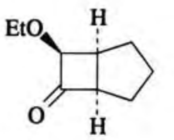
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (67)	5, 430, 431
	Cl_3CCOCl	Zn, Et_2O, ultrasound	" (70)	424
	MeCHBrCOCl	Et_3N, Et_2O	 (—)	432
	MeCHClCOCl	Et_3N, Et_2O	 (77)	416, 432
	 $(CF_3)_2C=C=O$	175°, 8 h	(—)	84
	$EtOCH_2COCl$	Et_3N	 (56)	391

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

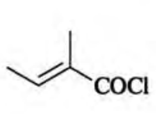
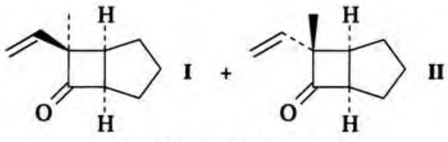
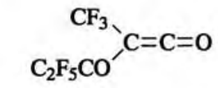
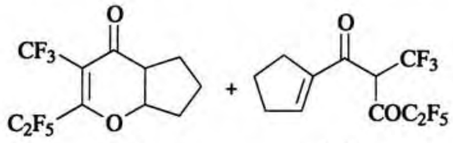
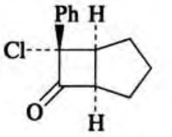
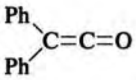
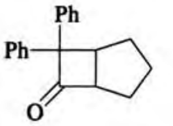
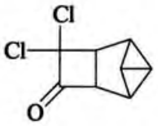
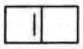
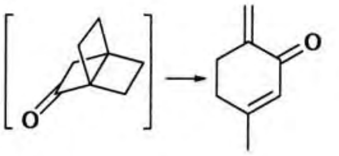
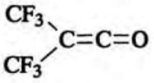
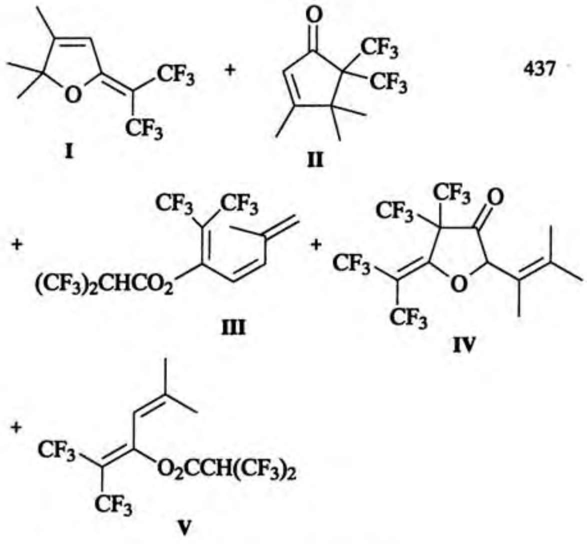
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 I + II (28), I:II = 3:7	409
	 $(CF_3)(C_2F_5CO)C{=}C{=}O$	180°, 8 h	 (—) (—)	346
	PhCHClCOCl	Et_3N	 (—)	433
	 $Ph_2C{=}C{=}O$	MeCN, 100°, 9 d	 (62)	386
C_6 	$Cl_2CHCOCl$	Et_3N, Et_2O	 (70)	434, 435

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	1. CH_2Cl_2, -78° 2. Al_2O_3	 (—)	436
	 $(CF_3)_2C{=}C{=}O$	25°		437

Solvent	I	II	III	IV	V
Cyclohexane	(63)	(27)	(5)	(1)	(4)
$Cl(CH_2)_2Cl$	(61)	(9)	(11)	(18)	(1)
MeCN	(21)	(1)	(0)	(72)	(6)

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

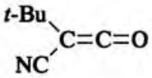
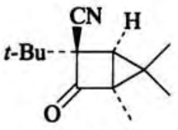
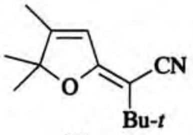
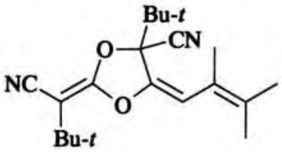
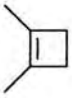
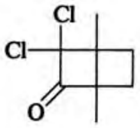
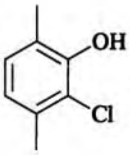
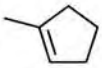
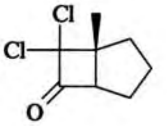
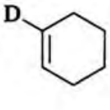
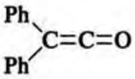
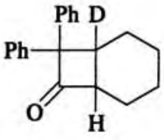
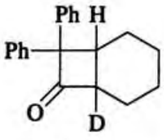
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, 25°, 15 min	 (28) +  (7) +  (40)	429
	Cl_3CCOCl	Zn, Et_2O	 (17) +  (3)	438
	Cl_3CCOBr	Zn, Et_2O	 (18)	439, 440
	 $Ph_2C{=}C{=}O$	100°, 10 d	 (—) +  (—)	53

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

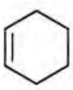
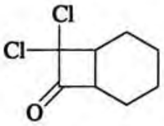
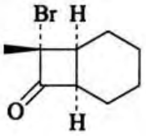
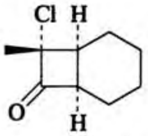
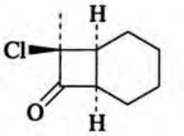
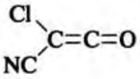
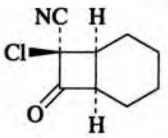
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N	 (57)	431, 441
	Cl_3CCOBr	Zn, Et_2O	" (70)	400, 439
	Cl_3CCOCl	Zn, Et_2O	" (90)	400
	Cl_3CCOCl	Zn-Cu, Et_2O	" (52)	403
	MeCHBrCOCl	Et_3N	 (—)	432
	MeCHClCOCl	Et_3N, C_6H_{14}	 I +  II I + II (26), I:II = 1:5.5	442, 416
	 $Cl(NC)C{=}C{=}O$	PhMe, reflux	 (64)	443, 312

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

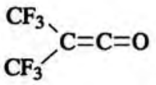
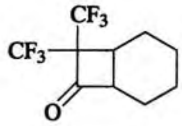
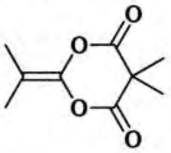
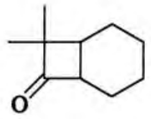
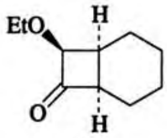
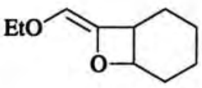
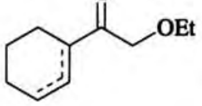
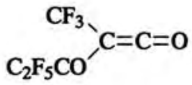
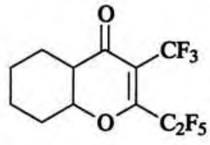
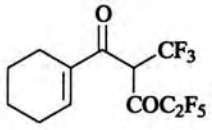
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(CF_3)_2C=C=O$	100°, 7 weeks	 (—)	84
		PhMe, 110°, K_2CO_3 (cat.)	 (32)	293
	$EtOCH_2COCl$	Et_3N	 (46) +  (18) +  (18)	391
	 $CF_3(C_2F_5CO)C=C=O$	95°, 22 d	 (13) +  (10)	346

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

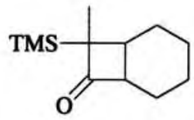
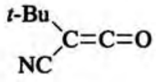
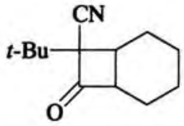
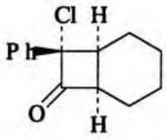
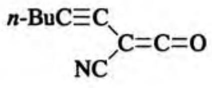
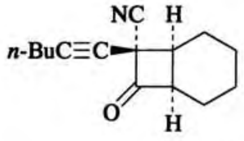
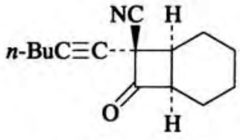
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCOCOTMS	hν, C_5H_{10}	 (—)	307
	 $t\text{-Bu}(NC)C=C=O$	C_6H_6, reflux, 3 h	 (63)	353
	PhCHClCOCl	Et_3N	 (70)	433
	 $n\text{-BuC}\equiv C(NC)C=C=O$	C_6H_6, reflux	 I +  II I + II (44), I:II = 4:1	402

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

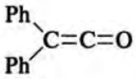
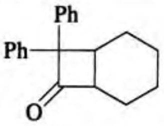
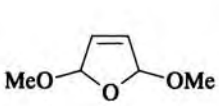
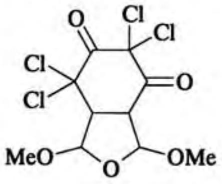
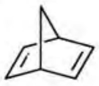
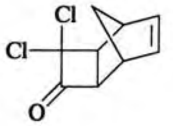
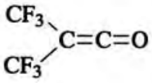
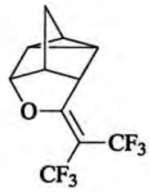
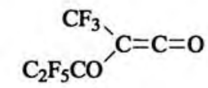
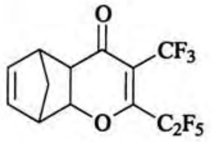
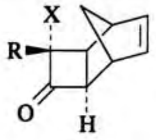
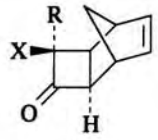
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	100°, 10 d	 (60)	444, 412, 445
	Cl_3CCOCl	Zn, Et_2O	 (—)	427
C_7 	$Cl_2CHCOCl$	Et_3N	 (25)	431, 441
	 $(CF_3)_2C=C=O$	100°	 (81)	84
	 $(CF_3)(C_2F_5CO)C=C=O$	Phenothiazine, 60°, 2 h	 (—)	346

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCHXCOCl	Et_3N, solvent	 I  II	446

Solvent	R	X	I + II	I:II
C_6H_{12}	Me	Cl	(16)	100:0
MeCN	Me	Cl	(7)	40:60
C_6H_{12}	Me	Br	(17)	100:0
MeCN	Me	Br	(5)	0:100
C_6H_{12}	Et	Cl	(14)	100:0
MeCN	Et	Cl	(8)	44:56
C_6H_{12}	*i*-Pr	Cl	(6)	100:0
MeCN	*i*-Pr	Cl	(1)	100:0
C_6H_{12}	*t*-Bu	Br	No 1:1 adduct	
MeCN	*t*-Bu	Br	No 1:1 adduct	

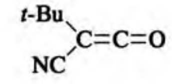
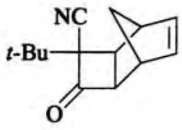
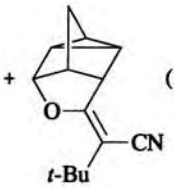
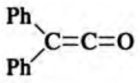
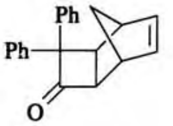
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(t\text{-Bu})(NC)C=C=O$	C_6H_6, 78°	 (26) +  (19)	392, 447
	 $Ph_2C=C=O$	C_6H_6, 65°, 12 d	 (60)	418

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

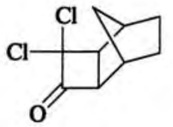
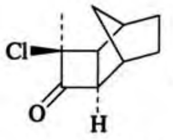
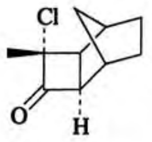
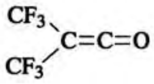
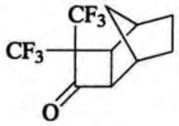
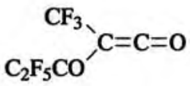
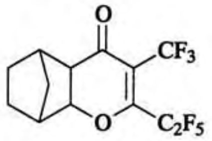
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_{12}	 (10)	441
	Cl_3CCOCl	Zn, Et_2O	" (64)	400
	"	Zn, Et_2O, $POCl_3$	" (70)	298
	"	Zn, Et_2O, ultrasound	" (75)	424
	MeCHClCOCl	Et_3N, MeCN	 I +  II I + II (5), I:II = 1:1	446
	MeCHClCOCl	Et_3N, C_6H_{12}	II (12)	446
	 $(CF_3)_2C=C=O$	175°, 8 h	 (97)	84
	 $(CF_3)(C_2F_5CO)C=C=O$	60°, 16 h	 (67)	346

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

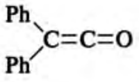
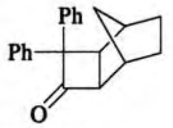
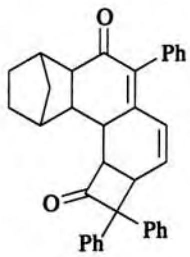
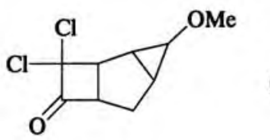
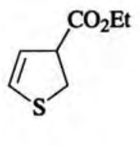
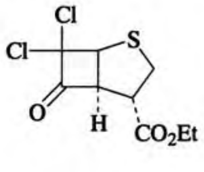
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_6, reflux 14 d	 I (84)	448
		Excess Olefin, 70°, 2 d	I (45-68) +  (10-16)	448
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (80)	89
	$Cl_2CHCOCl$	Et_3N, CCl_4	 (33)	449

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

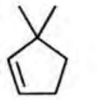
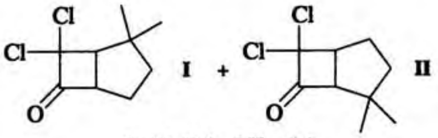
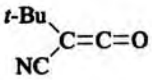
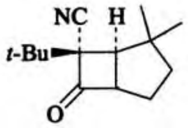
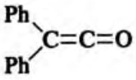
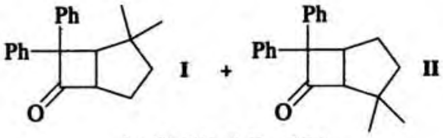
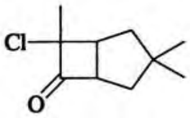
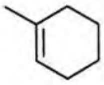
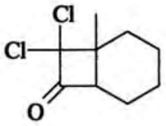
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N	 I + II (51), I:II = 5:1	450, 451
	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, 78°	 (—)	450
	 $Ph_2C{=}C{=}O$	100°, 11 d	 I + II (90), I:II = 5.7:1	450
	MeCHClCOCl	Et_3N	 (—)	452
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (83)	82,83

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

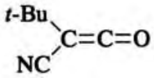
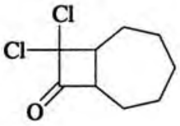
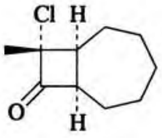
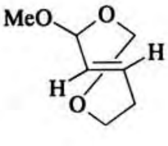
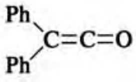
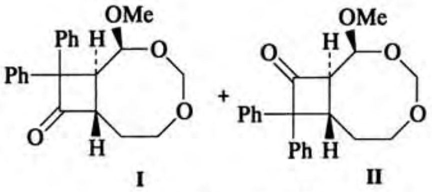
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	" (79)	298
	"	Zn, Et_2O	" (80)	400, 439, 440
	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, 78°	(—)	55
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (85)	83, 453
	MeCHClCOCl	Et_3N, C_6H_{14}	 (66)	416
	 $Ph_2C{=}C{=}O$	-45 to 60°	 I + II (—), I:II = 7:1	454

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

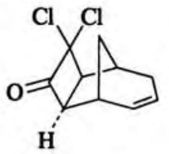
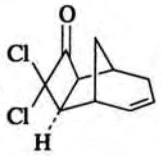
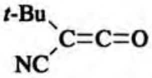
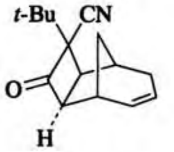
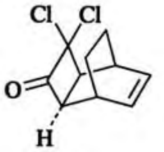
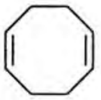
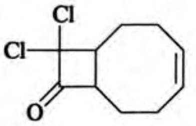
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	Cl_3CCOCl	Zn, Et_2O	 (14) +  (70)	455
	 $(t\text{-Bu})(NC)C{=}C{=}O$	C_6H_6, 78°	 (—)	394
	Cl_3CCOCl	Zn, Et_2O	 (86)	76
	$Cl_2CHCOBr$	Et_3N, C_6H_{14}	 (53)	403
	Cl_3CCOCl	Zn, Et_2O, ultrasound	" (70)	424
	Cl_3CCOCl	Zn-Cu, Et_2O	" (60)	456, 453

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

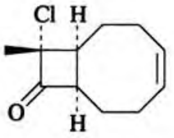
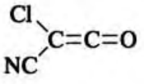
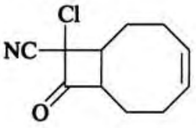
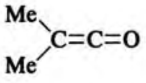
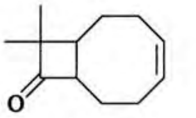
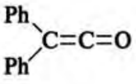
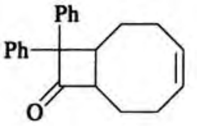
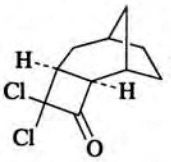
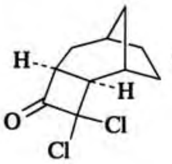
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCHClCOCl	Et_3N, C_6H_{14}	 (50)	416
	 $(Cl)(NC)C{=}C{=}O$	PhMe, reflux	 (78)	443
	 $Me_2C{=}C{=}O$	—	 (55)	457
	 $Ph_2C{=}C{=}O$	60°, 1 h	 (—)	458
	Cl_3CCOCl	Zn, Et_2O	 (34) +  (34)	455
	Cl_3CCOCl	Zn, Et_2O	(—)	76

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

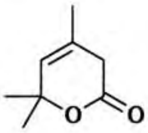
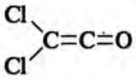
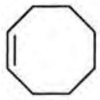
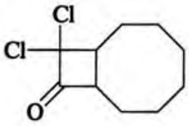
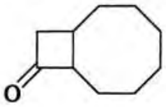
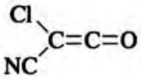
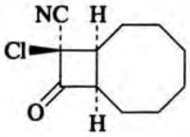
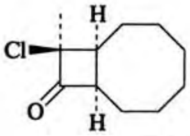
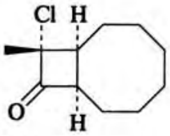
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Cl_2C=C=O$	—	(—)	459
	$Cl_2CHCOCl$	Et_3N	 (50)	57
	MeCOCl	Et_3N	 (27)	406
	 $Cl(NC)C=C=O$	PhMe, reflux	 (72)	443
	MeCHClCOCl	Et_3N, C_6H_{14}, 25°	 I +  II I + II (15), I:II = 5:1	442
	MeCHClCOCl	Et_3N, C_6H_{14}, 25°	II (83)	416

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

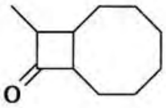
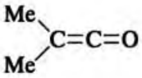
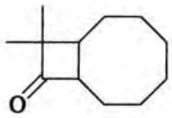
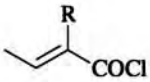
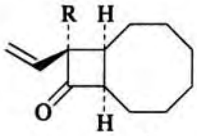
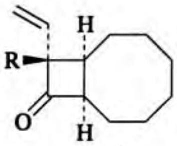
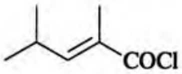
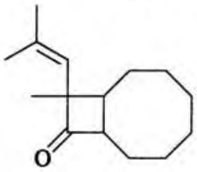
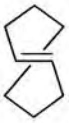
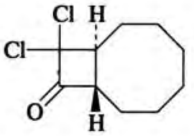
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtCOCl	Et_3N	 (17)	460
	 $Me_2C=C=O$	70-75°, 12 h	 (77)	457
		Et_3N	 +  I II R = Me, I + II (60), I:II = 1:3 R = Et, I + II (52), I:II = 15:85	409
		Et_3N	 (33)	409
	$Cl_2CHCOCl$	Et_3N	 (100)	57

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

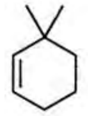
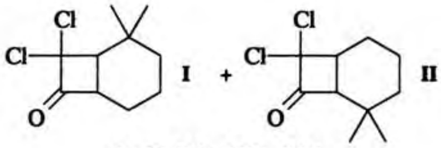
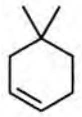
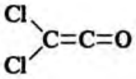
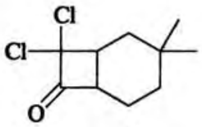
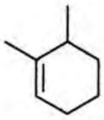
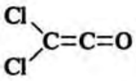
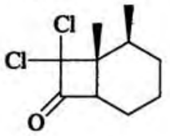
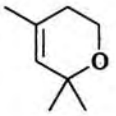
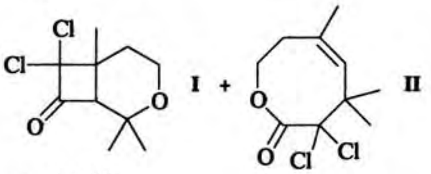
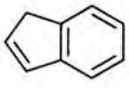
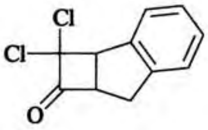
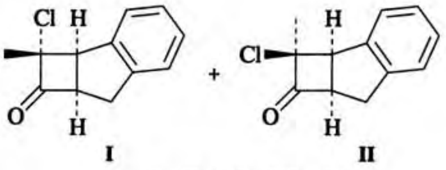
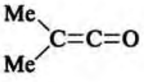
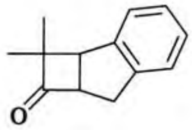
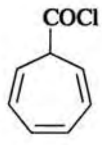
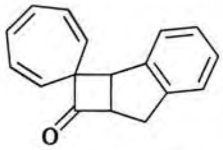
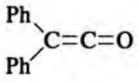
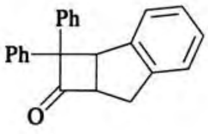
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N	 I + II (54), I:II = 1:2.6	450
	 $Cl_2C{=}C{=}O$	—	 (—)	451
	 $Cl_2C{=}C{=}O$	—	 (89)	461
	Cl_3CCOCl	Zn, Et_2O, $POCl_3$		462
	Cl_3CCOCl	Zn, glyme	" (50-60)	462
C_9 	$Cl_2CHCOCl$	Et_3N	 (41)	431, 463, 441
	Cl_3CCOBr	Zn, Et_2O	" (60-70)	439
	Cl_3CCOCl	Zn, Et_2O, ultrasound	" (80)	424
	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	" (81)	298
	MeCHClCOCl	Et_3N, C_6H_{14}	 I + II (78), I:II = 5:1	46
	 $Me_2C{=}C{=}O$	—	 (64)	457
		Et_3N, Et_2O	 (24)	464
	 $Ph_2C{=}C{=}O$	120°, 4 h	 (62)	465

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

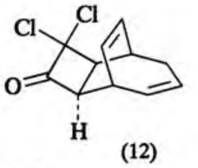
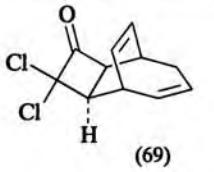
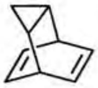
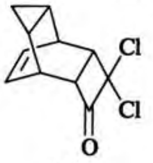
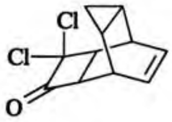
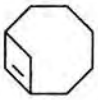
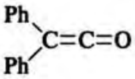
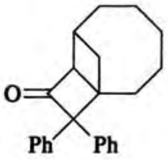
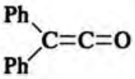
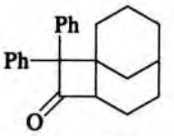
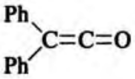
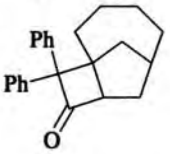
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O	 (12) +  (69)	455
	Cl_3CCOCl	Zn, Et_2O	 (74) +  (12)	76
	 $Ph_2C=C=O$	rt, 2 h	 (95)	77
	 $Ph_2C=C=O$	C_6H_6, rt	 (77)	466
	 $Ph_2C=C=O$	C_6H_6, rt	 (97)	466

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

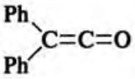
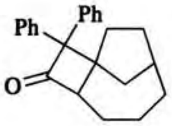
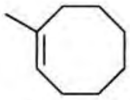
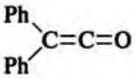
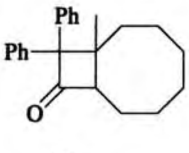
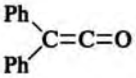
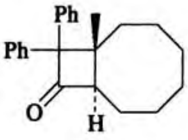
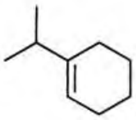
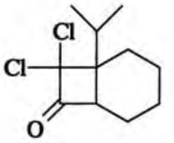
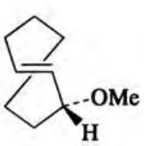
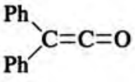
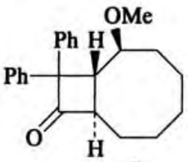
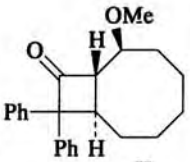
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_6, rt	 (83)	466
	 $Ph_2C=C=O$	C_6H_6, 120°, 72 h	 (78)	466
	 $Ph_2C=C=O$	C_6H_6, rt, 10 min	 (87)	466
	Cl_3CCOBr	Zn, Et_2O	 (—)	439
	 $Ph_2C=C=O$	-45 to 60°	 **I**  **II** **I** + **II** (—), **I**:**II** = 1:5	454

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

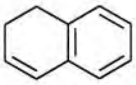
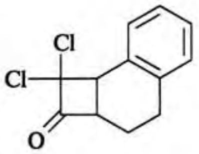
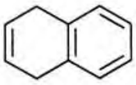
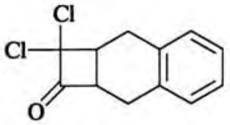
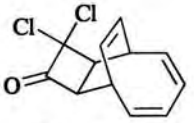
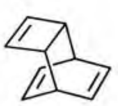
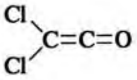
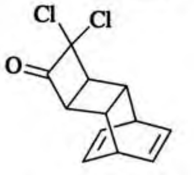
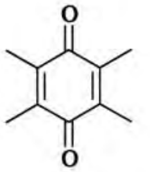
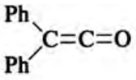
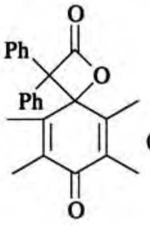
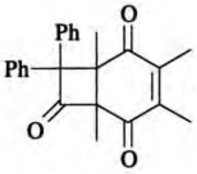
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	Cl_3CCOBr	Zn, Et_2O	 (71)	439
	Cl_3CCOBr	Zn, Et_2O	 (56)	439
	Cl_3CCOCl	Zn, Et_2O	 (95)	455
	 $Cl_2C=C=O$	—	 (60)	329
	 $Ph_2C=C=O$	*h*ν, Pyrex, C_6H_6	 (49) +  (25)	153

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

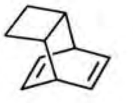
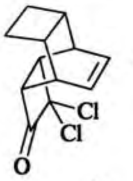
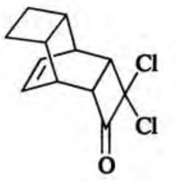
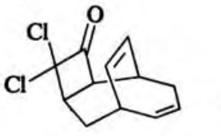
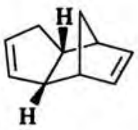
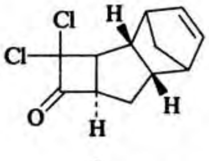
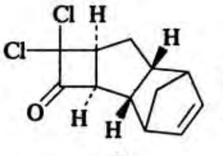
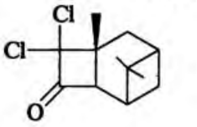
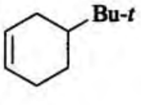
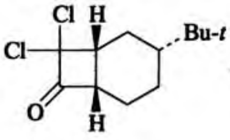
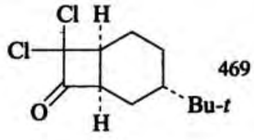
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O	 (14) +  (62)	76
	Cl_3CCOCl	Zn, Et_2O	 (86)	455
	$Cl_2CHCOCl$	Et_3N	 I +  II I + II (86), I:II = 19:81	467, 431, 468
	Cl_3CCOCl	Zn, Et_2O	 (16)	400
	Cl_3CCOBr	Zn	 (—) +  (—)	469

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

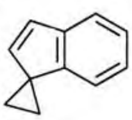
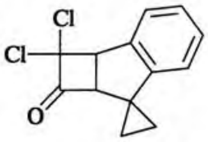
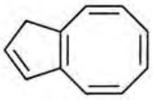
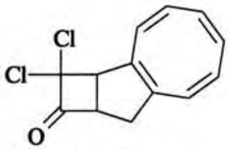
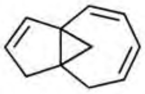
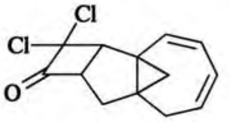
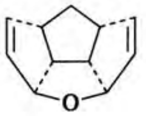
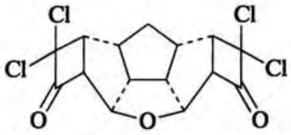
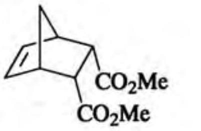
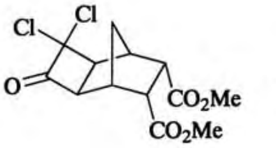
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (53)	470
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (89)	471
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (55)	472
	Cl_3CCOCl	Zn-Cu, Et_2O	 (35-40)	473, 474, 424
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (65)	475

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

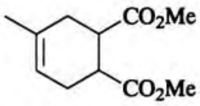
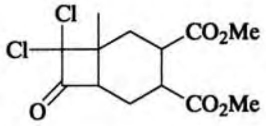
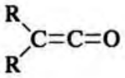
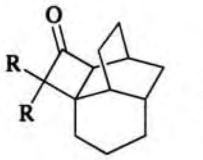
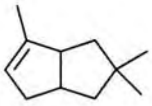
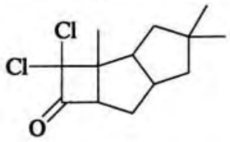
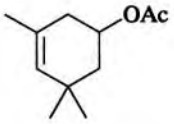
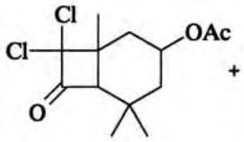
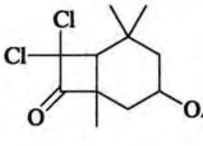
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (65)	476
	 $R_2C{=}C{=}O$	C_6H_6, rt	 R = H (25) R = Ph (38)	477, 478
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (60)	452
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 +  I II I + II (63), I:II = 1.8:1	476

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

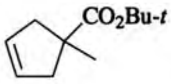
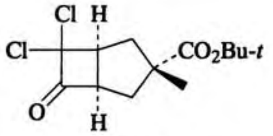
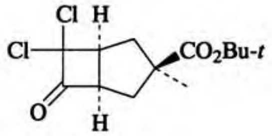
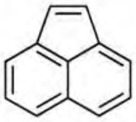
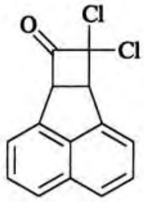
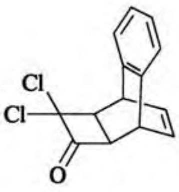
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (50) +	479
			 (18)	
C_{12}				
	$Cl_2CHCOCl$	Et_3N, PhMe	 (10)	480, 481, 63
	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	" (50-60)	482
	Cl_3CCOCl	Zn-Cu, Et_2O	 (89)	76

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

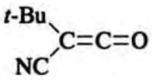
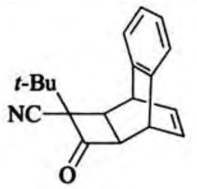
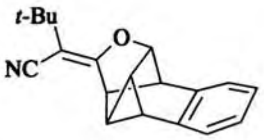
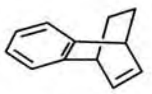
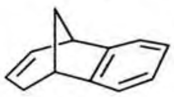
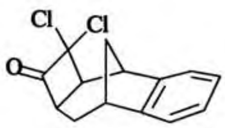
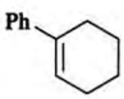
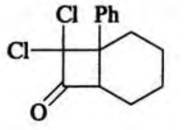
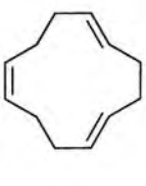
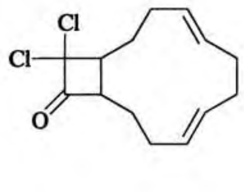
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(t\text{-Bu})(NC)C{=}C{=}O$	C_6H_6, 78°	 (33) +	394
			 (66)	
	Cl_3CCOCl	Zn, Et_2O	(—)	76
	Cl_3CCOCl	Zn, Et_2O	 (77)	455
	Cl_3CCOBr	Zn, Et_2O	 (61)	439, 440
	Cl_3CCOCl	Zn, Et_2O, ultrasound	 (90)	424

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

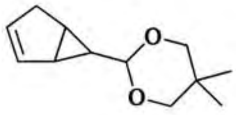
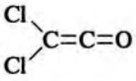
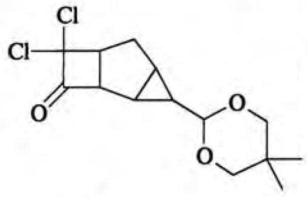
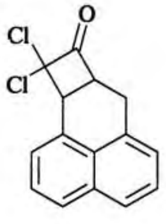
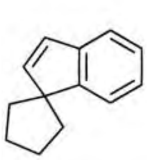
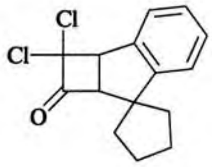
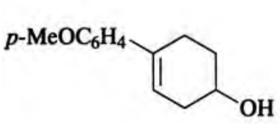
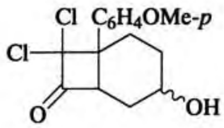
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Cl_2C=C=O$	—	 (81)	483
C_{13} 	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (—)	484
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (58)	470
	Cl_3CCOBr	Zn-Cu, Et_2O	 (56)	485

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

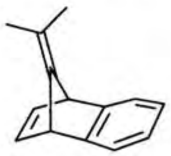
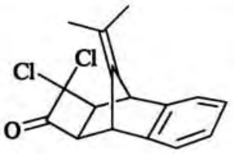
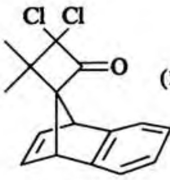
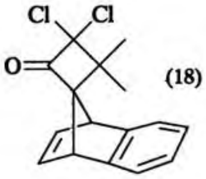
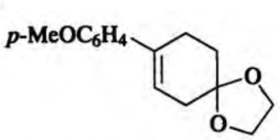
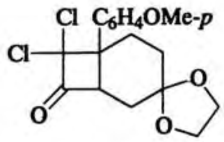
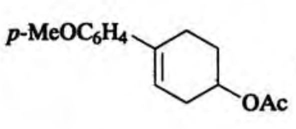
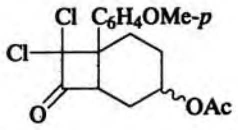
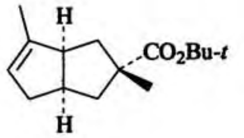
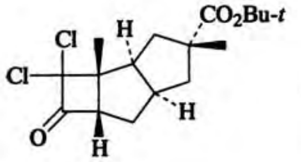
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	Cl_3CCOCl	Zn-Cu, Et_2O, $POCl_3$	 (27) +  (13) +  (18)	426
C_{15} 	Cl_3CCOBr	Zn-Cu, Et_2O	 (—)	485
	Cl_3CCOBr	Zn-Cu, Et_2O	 (85)	485
	Cl_3CCOCl	Zn-Cu, $POCl_3$	 (68)	479

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

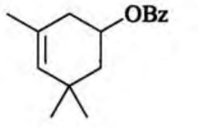
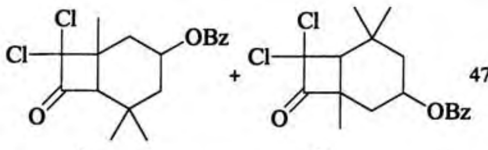
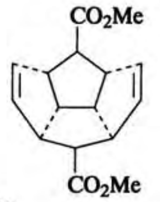
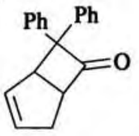
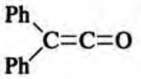
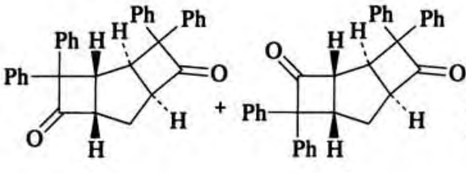
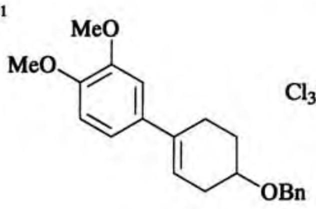
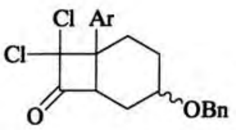
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	 I II I + II (61), I:II = 1.85:1	476
	Cl_3CCOCl	Zn-Cu, $POCl_3$	(—)	486
C_{19} 	 $Ph_2C{=}C{=}O$	130°, 11 d	 (—) (—)	487, 445
C_{21} 	Cl_3CCOBr	Zn-Cu, Et_2O	 (80)	485

TABLE IV. [2+2] CYCLOADDITION OF KETENES TO CYCLIC OLEFINS (*Continued*)

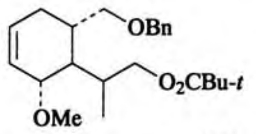
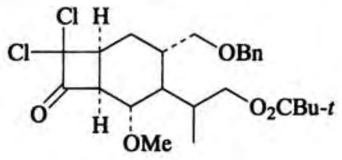
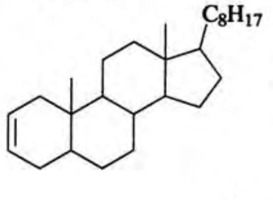
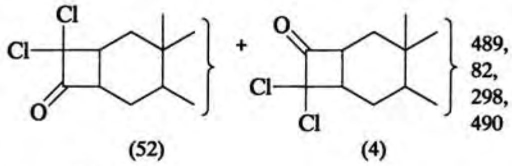
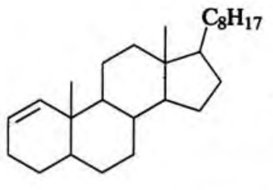
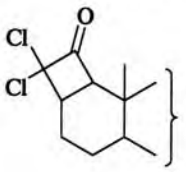
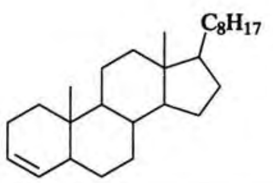
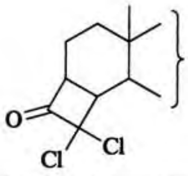
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	Cl_3CCOCl	Zn-Cu, Et_2O	 (44)	488
	Cl_3CCOBr	Zn, Et_2O	 (52) (4)	489, 82, 298, 490
	Cl_3CCOBr	Zn, Et_2O	 (58)	489
	Cl_3CCOBr	Zn, Et_2O	 (54)	489

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES

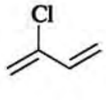
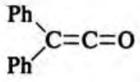
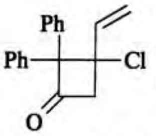
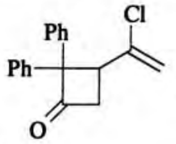
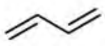
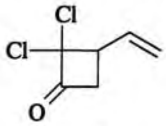
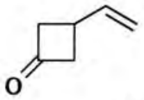
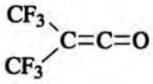
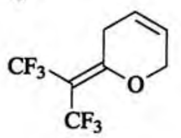
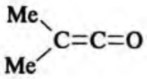
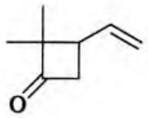
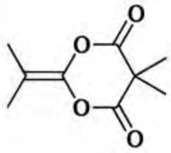
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	 $Ph_2C{=}C{=}O$	CCl_4	 I +  II I + II (—), I:II = 4:1	491
	$Cl_2CHCOCl$	Et_3N, C_6H_{12}	 (—)	431
	$CH_2{=}C{=}O$	100°, 2 h	 (—)	87
	 $(CF_3)_2C{=}C{=}O$	100°, 60 h	 (78)	84, 231, 85
	 $Me_2C{=}C{=}O$	100°, 30 min	 (—)	492
		K_2CO_3 (cat.) PhMe, 140°	" (50)	293

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

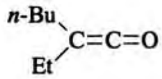
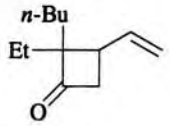
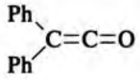
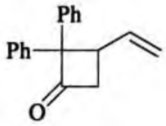
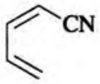
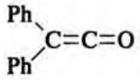
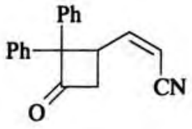
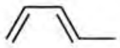
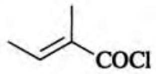
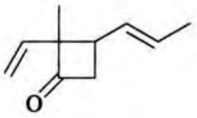
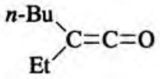
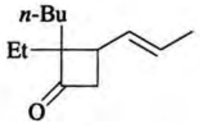
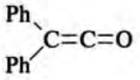
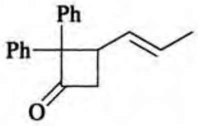
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(n\text{-}Bu)(Et)C{=}C{=}O$	150°	 (45)	493
	 $Ph_2C{=}C{=}O$	THF, C_7H_{16}, 30°	 (55)	491, 396
C_5 	 $Ph_2C{=}C{=}O$	4 weeks	 (89)	494, 36, 495, 496
		Et_3N	 (—)	305
	 $(n\text{-}Bu)(Et)C{=}C{=}O$	180°	 (64)	493
	 $Ph_2C{=}C{=}O$	20°, 4 d	 (95)	36, 495, 494, 496, 412

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

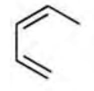
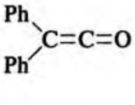
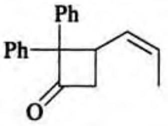
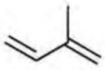
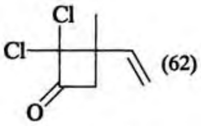
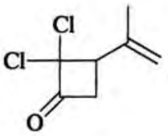
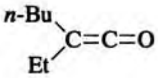
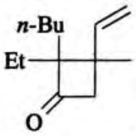
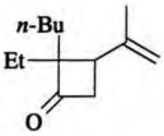
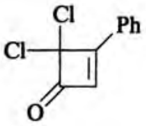
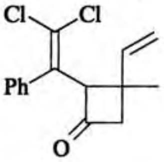
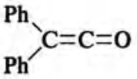
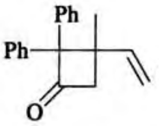
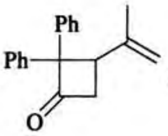
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	20°, 4 d	 (99)	494, 36, 495
	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	 (62) +  (19)	497
	 $n\text{-}Bu(Et)C{=}C{=}O$	150°, 4 h	 I +  II I + II (45)	493
		hν, C_6H_6	 (70)	306
	 $Ph_2C{=}C{=}O$	16 d	 (64) +  (28)	494, 491, 495, 36

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

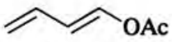
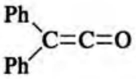
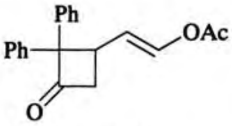
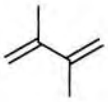
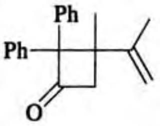
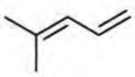
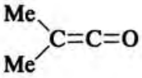
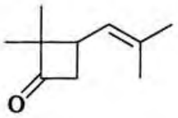
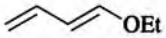
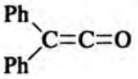
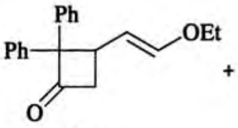
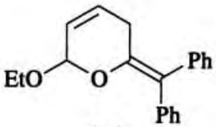
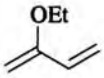
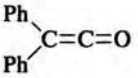
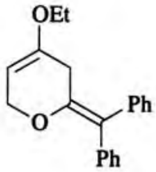
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 $Ph_2C{=}C{=}O$	42°	 (—)	495, 496
	"	100°, 10 h	Adduct, mp 146°	396
	"	14 weeks	 (86)	36, 494, 396, 412
	 $Me_2C{=}C{=}O$	125°	 (60)	498
	 $Ph_2C{=}C{=}O$	C_6H_6	 (—) +  (—)	496, 495
	 $Ph_2C{=}C{=}O$	100°, 16 h	 (—)	496

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

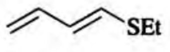
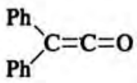
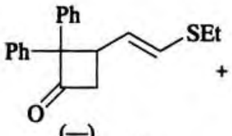
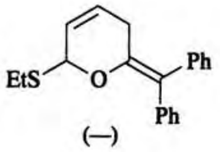
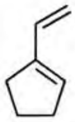
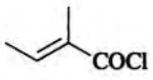
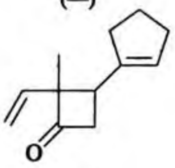
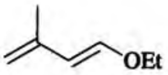
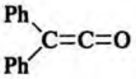
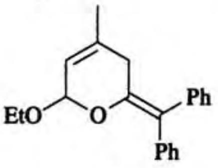
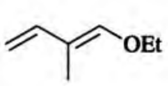
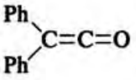
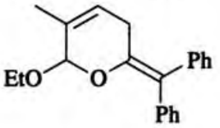
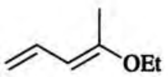
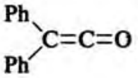
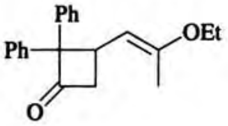
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		42°	 (—) +  (—)	495
C_7				
		Et_3N	 (—)	305
		—	 (—)	496, 495
		—	 (—)	496, 495
		—	 (—)	496, 495

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

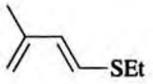
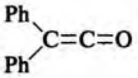
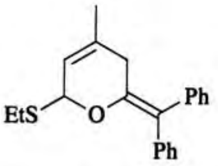
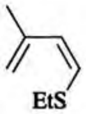
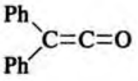
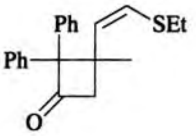
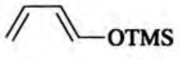
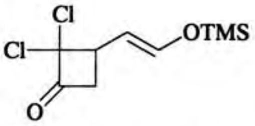
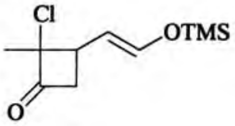
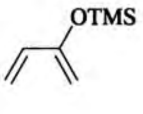
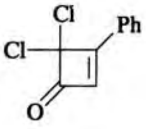
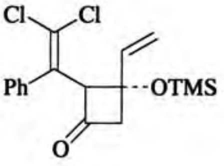
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		42°	 (—)	496, 495
		42°	 (—)	496, 495
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (71)	499
	MeCHClCOCl	Et_3N, C_6H_{14}	 (66)	499
		hν, C_6H_6	 (50)	306

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

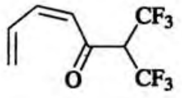
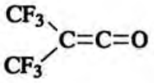
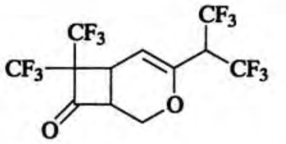
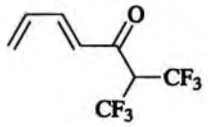
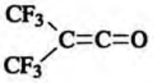
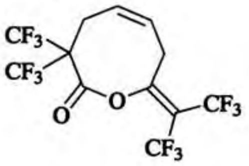
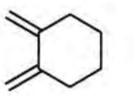
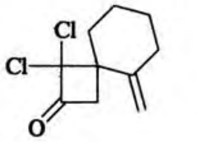
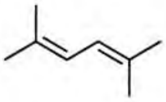
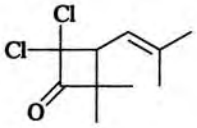
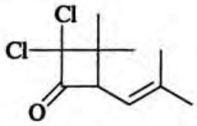
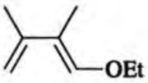
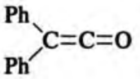
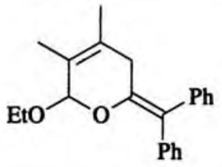
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	 $(CF_3)_2C=C=O$	100°, 16 h	 (—)	84
	 $(CF_3)_2C=C=O$	100°	 (—)	85
	Cl_3CCOCl	Zn, Et_2O, $POCl_3$	 (61)	500
	Cl_3CCOCl	Zn, Et_2O	 +  (30) (13)	400
	 $Ph_2C=C=O$	42°	 (—)	495

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

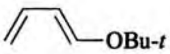
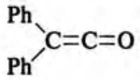
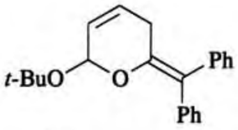
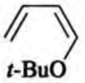
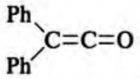
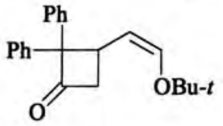
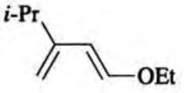
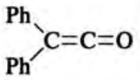
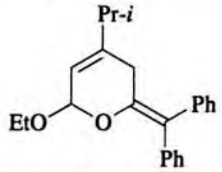
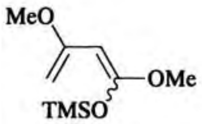
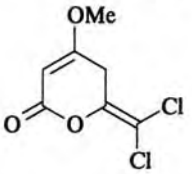
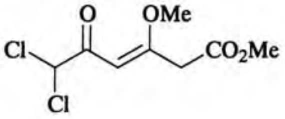
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_6, 48 h	 (—)	86
	 $Ph_2C=C=O$	C_6H_6, 48 h	 (—)	86
C_9				
	 $Ph_2C=C=O$	42°	 (—)	495
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (30) +  (34)	235

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

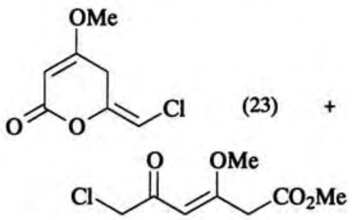
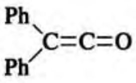
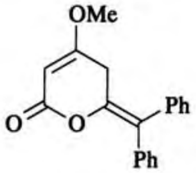
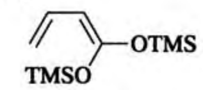
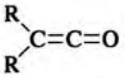
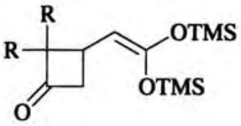
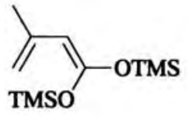
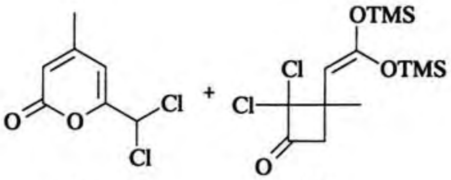
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$ClCH_2COCl$	Et_3N, Et_2O	 (23) +	235
	 $Ph_2C=C=O$	1. Et_2O 2. MeOH, HCl	 (56)	235
C_{10} 	 $R_2C=C=O$ R = Cl, Ph	—	 (—)	235
C_{11} 	$Cl_2CHCOCl$	Et_3N, Et_2O	 (31) (55)	235

TABLE V. [2+2] CYCLOADDITION OF KETENES TO ACYCLIC DIENES (*Continued*)

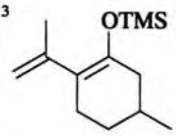
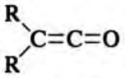
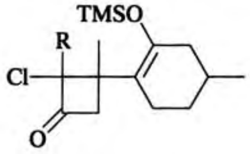
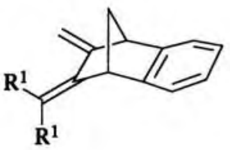
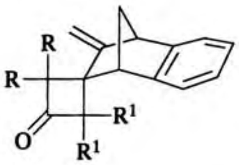
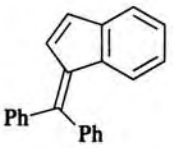
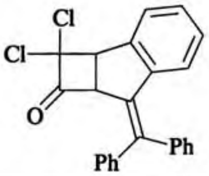
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	 $R_2C=C=O$ R = Cl, Me	Et_3N	 R = Cl (58) R = Me (49)	499
C_{16} 	$R_2ClCCOCl$	Zn, Et_2O, $POCl_3$	 R = Cl, R^1 = H (43) R = H, R^1 = Cl (14)	501
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (22)	502, 503

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES

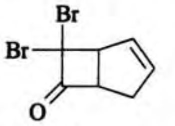
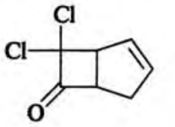
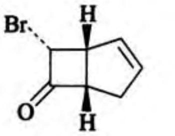
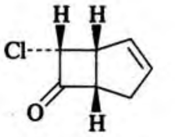
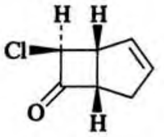
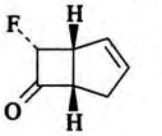
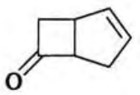
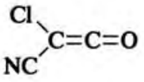
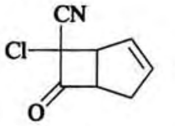
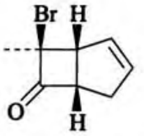
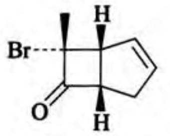
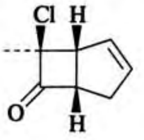
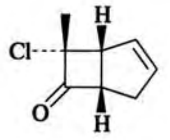
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5 	$Br_2CHCOCl$	Et_3N, C_6H_{14}	 (58)	504
	$Cl_2CHCOCl$	Et_3N	 (72)	319, 505, 6, 5, 318, 506, 83, 507, 508
	$BrCH_2COBr$	Et_3N, Et_2O	 (5)	509, 328
	$ClCH_2COCl$	Et_3N	 +  *endo* *exo* *endo*:*exo* = >97:<3	38, 510, 509, 511, 512
	FCH_2COCl	Et_3N, Et_2O, -78°	 (40)	509, 328, 46

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	rt	 (—)	513- 515
	 $Cl(NC)C{=}C{=}O$	PhMe, 103°, 1.75 h	 (30)	312
	MeCHBrCOCl	Et_3N	 I +  II I + II (63), I:II = 56:44	38, 516- 518
	MeCHClCOCl	Et_3N, solvent	 I +  II	

Solvent	I + II	I:II	Ref.
C_6H_{14}	(75)	81:19	516
C_6H_{14}	(67)	80:20	38
C_5H_{12}	(88)	73:27	511
Et_3N	(32)	67:33	517
$CHCl_3$	(40)	62:38	517
MeCN	(62)	37:63	516

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

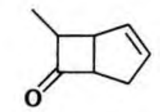
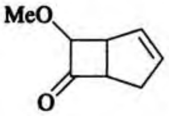
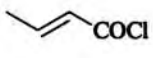
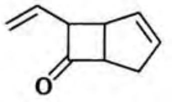
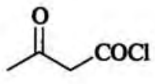
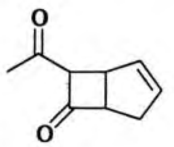
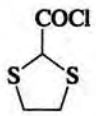
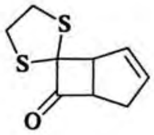
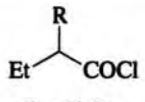
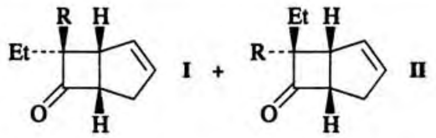
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	EtCOCl	Et_3N, C_6H_{14}	 (20) *endo*:*exo* = 98:2	38, 509, 519
	$MeOCH_2COCl$	Et_3N	 (9) *endo*:*exo* = >95:<5	38
		Et_3N, $CHCl_3$	 (38) *endo*:*exo* = 82:18	411, 305
		Et_3N	 (56) *endo*:*exo* = 94:6	520
		Et_3N	 (84)	521

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 R = Cl, Br	Et_3N, solvent		516, 518, 511, 510

R	Solvent	I + II	I:II
Br	C_6H_{14}	(70)	62:38
Br	MeCN	(54)	21:79
Cl	C_6H_{14}	(77)	84:16
Cl	C_5H_{12}	(70)	89:11
Cl	MeCN	(77)	52:48

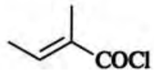
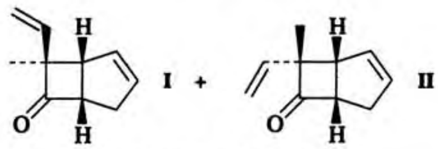
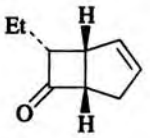
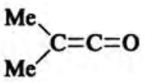
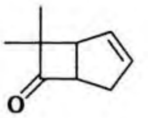
		Et_3N, $CHCl_3$	 I + II (59), I:II = 92:8	411
	n-PrCOBr	Et_3N, CCl_4	 (34)	509
	 $Me_2C{=}C{=}O$	rt, 16 h	 (77)	38,522- 524

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

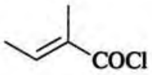
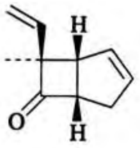
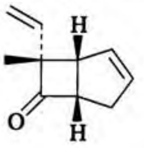
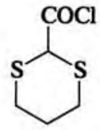
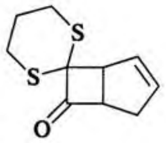
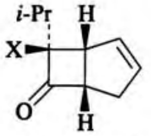
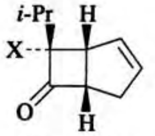
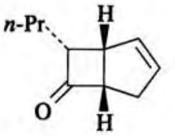
<table>
<tr><th>Reactant</th><th>Ketene or Ketene Source</th><th>Conditions</th><th>Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td></td><td></td><td>Et_3N, $CHCl_3$</td><td> (51) +  (27)</td><td>38</td></tr>
<tr><td></td><td></td><td>Et_3N, Et_2O</td><td> (70)</td><td>525</td></tr>
<tr><td></td><td><i>i</i>-PrCHXCOCl</td><td>Et_3N, solvent</td><td> I +  II
<table>
<tr><th>Solvent</th><th>X</th><th>I</th><th>II</th><th>Ref.</th></tr>
<tr><td>C_6H_{14}</td><td>Br</td><td>(55)</td><td>(21)</td><td>516</td></tr>
<tr><td>MeCN</td><td>Br</td><td>(17)</td><td>(29)</td><td>516</td></tr>
<tr><td>C_6H_{14}</td><td>Cl</td><td>(65)</td><td>(6)</td><td>516</td></tr>
<tr><td>—</td><td>Cl</td><td>(55)</td><td>(3)</td><td>510</td></tr>
<tr><td>C_5H_{12}</td><td>Cl</td><td>(55)</td><td>(3)</td><td>511</td></tr>
<tr><td>MeCN</td><td>Cl</td><td>(40)</td><td>(37)</td><td>516</td></tr>
</table></td><td></td></tr>
<tr><td></td><td><i>n</i>-BuCOCl</td><td>Et_3N</td><td> (—)</td><td>519</td></tr>
</table>

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

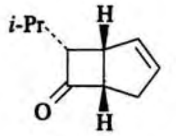
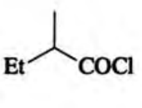
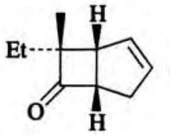
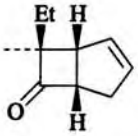
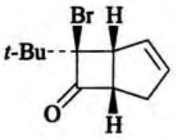
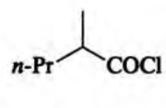
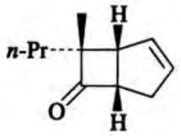
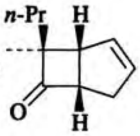
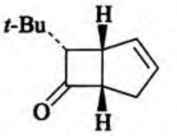
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	i-BuCOCl	Et_3N, $CHCl_3$	 (37)	509, 519
		Et_3N	 (43) +  (29)	38
	t-BuCHBrCOCl	Et_3N, solvent	 MeCN (54) C_6H_{14} (11)	516
		Et_3N, MeCN	 (47) +  (34)	516, 38
	t-$BuCH_2COCl$	Et_3N	 (22)	526, 519

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

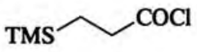
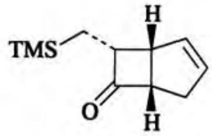
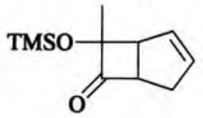
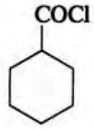
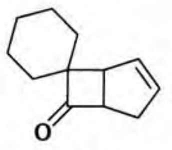
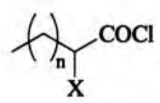
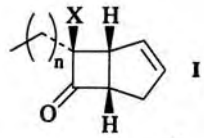
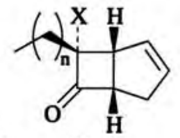
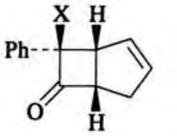
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et$_3$N, C$_6$H$_{14}$	 (65)	352
	MeCOCOTMS	hν, C$_5$H$_{12}$	 (—)	307
		Et$_3$N, C$_6$H$_6$	 (65)	527
		Et$_3$N, C$_6$H$_{14}$	 I +  II n X I II 2 Br (43) (27) 3 Br (25) (15) 2 Cl (50) (5)	528
	PhCHXCOCl	Et$_3$N	 X Yield (%) Br (53) Cl (95) H (26) Me (85)	529 511 38 529

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

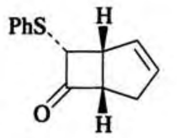
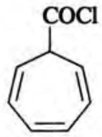
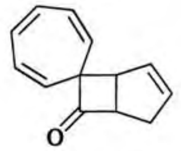
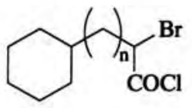
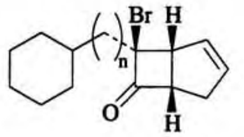
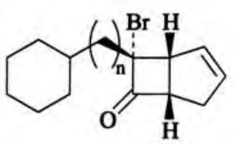
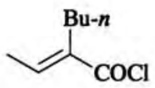
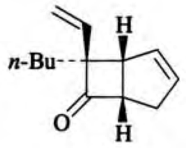
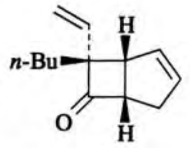
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	PhSCH$_2$COCl	Et$_3$N, C$_6$H$_{14}$	 (—)	521
		Et$_3$N, Et$_2$O	 (60)	424
		Et$_3$N, C$_6$H$_{14}$	 I +  II n I II 0 (62) (20) 1 (59) (24) 2 (66) (26)	528
		Et$_3$N, CHCl$_3$	 +  (54) (5)	411

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

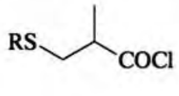
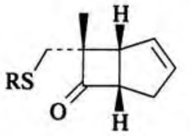
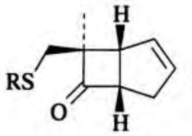
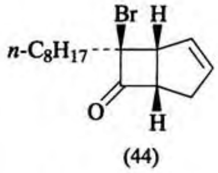
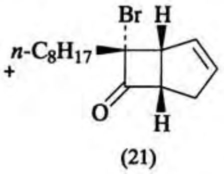
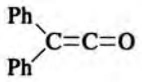
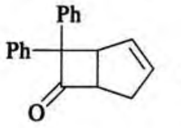
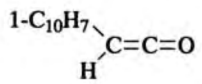
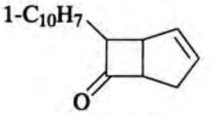
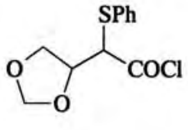
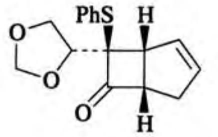
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, C_6H_{12}	 I +  II R I II Ph (56) (28) *t*-Bu (53) (26)	530, 521
	n-$C_8H_{17}CHBrCOCl$	Et_3N, C_6H_{12}	 +  (44) (21)	528
		C_6H_{14}, rt, 24 h	 (92)	445, 491, 531, 36, 412, 340, 444, 532
		—	 (—)	533
		Et_3N, Et_2O	 (57)	521

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

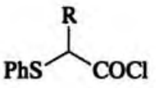
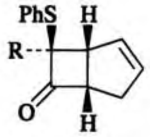
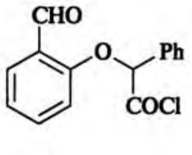
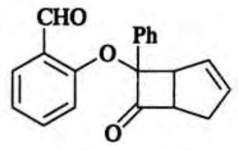
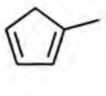
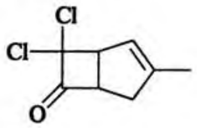
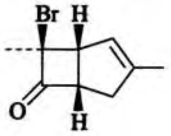
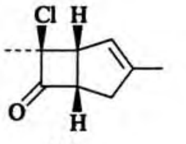
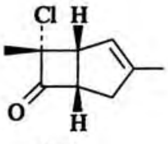
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, Et_2O	 R = *n*-C_7H_{15} (84) R = *n*-Bu (82)	521
		Et_3N, C_6H_6	 (—)	293
C_6 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (55)	528
	MeCHBrCOCl	Et_3N, C_6H_{14}	 (50)	528
	MeCHClCOCl	Et_3N, C_6H_{14}	 +  (60) (15)	528

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

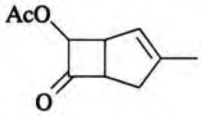
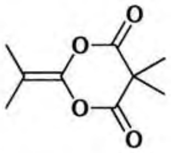
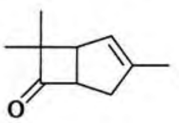
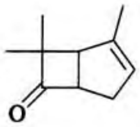
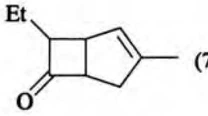
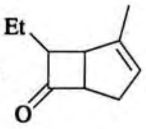
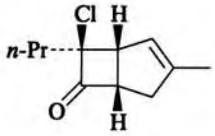
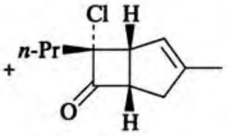
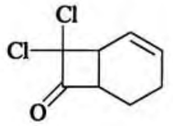
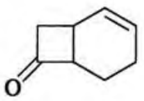
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$AcOCH_2COCl$	Et_3N	 (—)	520
		K_2CO_3	 (55) +  (17)	534
	n-$PrCOCl$	Et_3N, $CHCl_3$	 (76) +  (5)	534
	n-$PrCHClCOCl$	Et_3N, C_6H_{14}	 +  (55) (5)	528
	$Cl_2CHCOCl$	Et_3N	 (60)	431, 441, 88, 535
	$CH_2{=}C{=}O$	PhMe, 100°, 4 d	 (—)	514

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

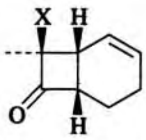
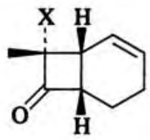
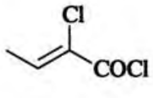
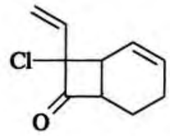
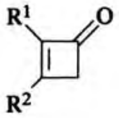
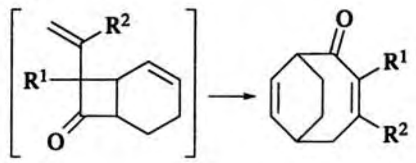
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$MeCHXCOCl$	Et_3N, solvent	 I +  II	
			Solvent X I II	
			C_6H_{14} Br (26) (14)	442
			C_6H_{14} Cl (42) (8)	442
			MeCN Cl (5) (40)	536
		Et_3N	 (—)	305
		80°, 60 h	 $R^1 = H, R^2 = Me$ (49) $R^1 = H, R^2 =$ n-Bu (33) $R^1 = R^2 = Me$ (91)	305

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

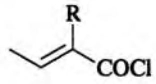
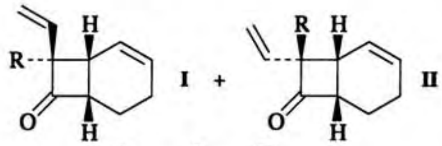
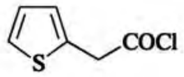
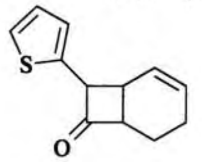
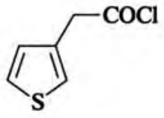
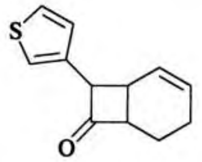
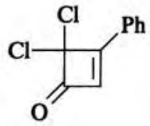
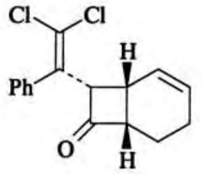
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, $CHCl_3$	 I + II R I II Me (37) (20) *n*-Bu (41) (1)	411
		Et_3N, PhMe	 (32)	537
		Et_3N, PhMe	 (33)	537
		*h*ν, C_6H_6	 (75)	306

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

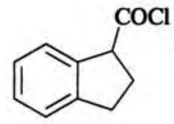
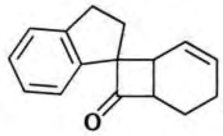
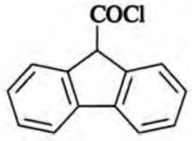
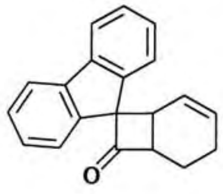
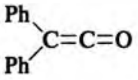
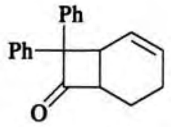
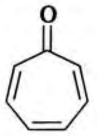
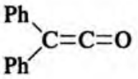
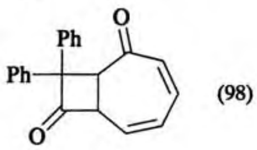
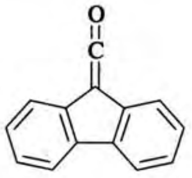
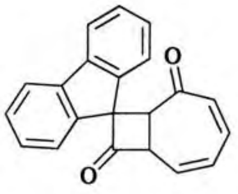
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, C_6H_6	 (99)	538
		Et_3N, C_6H_6	 (62)	538
	 $Ph_2C=C=O$	—	 (—)	412
C_7 	 $Ph_2C=C=O$	C_6H_6	 (98)	539
		—	 (63)	539

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

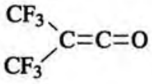
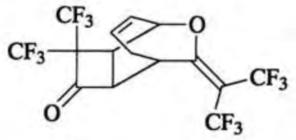
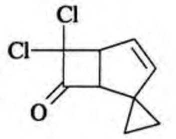
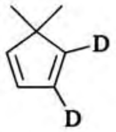
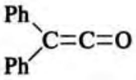
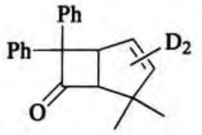
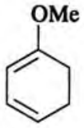
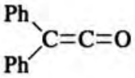
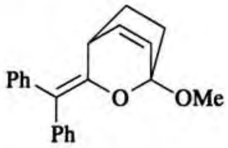
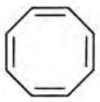
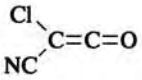
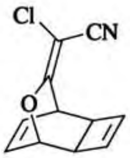
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $\overset{\mathrm{CF_3}}{\underset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{=C=O}$	100°, 16 h	 (68)	84
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (55)	525, 450
	 $\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}\mathrm{=C=O}$	C_6H_6, 78°	 (—)	52
	 $\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}\mathrm{=C=O}$	42°	 (—)	495
C_8 	 $\overset{\mathrm{Cl}}{\underset{\mathrm{NC}}{\mathrm{C}}}\mathrm{=C=O}$	PhMe, 109°	 (19)	443

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

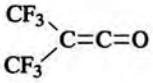
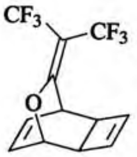
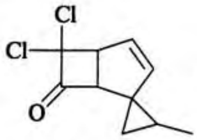
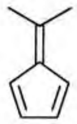
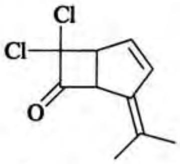
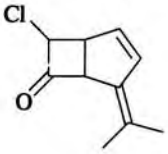
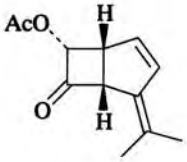
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $\overset{\mathrm{CF_3}}{\underset{\mathrm{CF_3}}{\mathrm{C}}}\mathrm{=C=O}$	100°, 3 d	 (36)	84
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (93)	470
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (96)	540
	$ClCH_2COCl$	Et_3N, C_6H_{14}	 (22)	540
	$AcOCH_2COCl$	Et_3N	 (—)	520

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

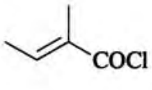
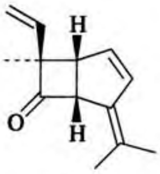
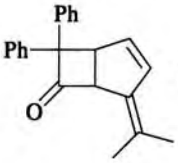
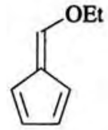
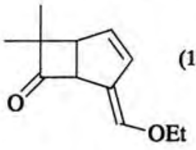
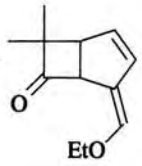
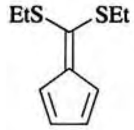
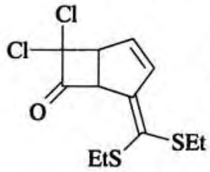
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 (—)	541
	$Ph_2C=C=O$	rt, 6 d	 (—)	372
	*i*-PrCOCl	Et_3N, C_6H_{14}	 (15) +  (45)	92
	$Cl_2CHCOCl$	Et_3N, Et_2O, -10°	 (—)	542

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

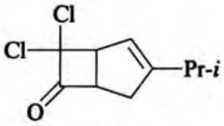
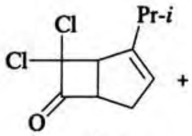
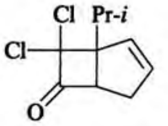
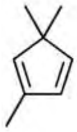
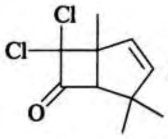
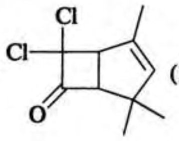
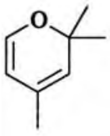
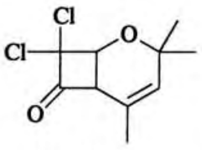
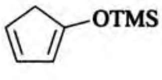
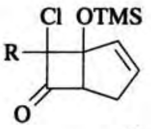
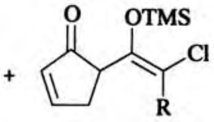
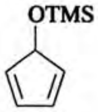
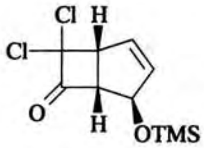
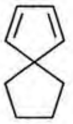
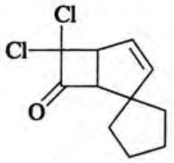
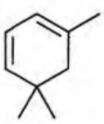
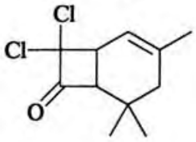
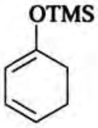
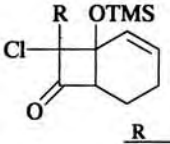
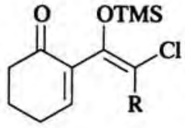
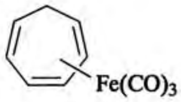
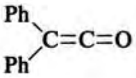
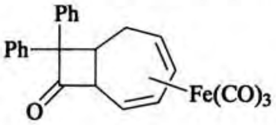
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (3) +  (23) +  (54)	543
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (13) +  (13)	459
	Cl_3CCOCl	Zn, $POCl_3$	 (45)	459
	RCHClCOCl	Et_3N	 I +  II R I II Cl (65) (22) Me (82) (0)	499

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N	 (69)	544, 545
C9 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (55)	470
	$Cl_2CHCOCl$	Et_3N, C_5H_{10}	 (53)	450, 451
	RCHClCOCl	Et_3N	 I +  II	499
C10 	 $Ph_2C=C=O$	C_6H_6, rt	 (25)	546

R	I	II
Cl	(51)	(17)
Me	(73)	(0)

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

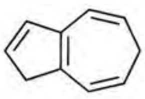
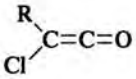
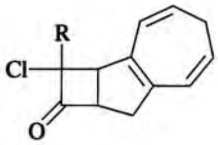
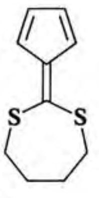
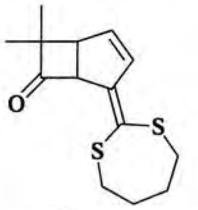
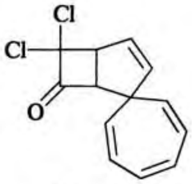
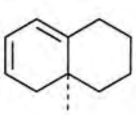
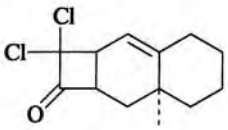
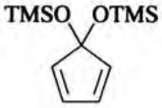
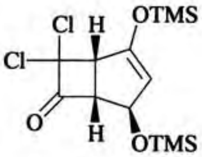
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $R(Cl)C=C=O$	C_6H_{14}	 R = H (22) R = Cl (84)	547
	*i*-PrCOCl	Et_3N, CH_2Cl_2	 (65)	92
C11 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (46)	471
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (70)	548
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (72)	549

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

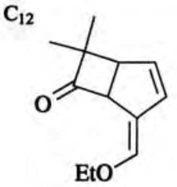
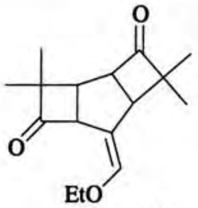
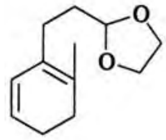
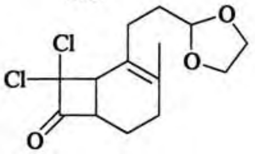
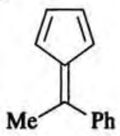
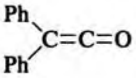
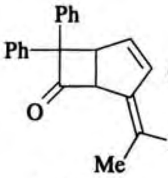
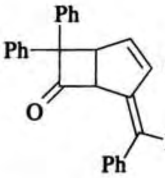
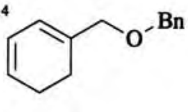
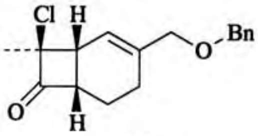
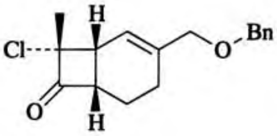
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 	*i*-PrCOCl	Et_3N, C_6H_{14}	 (57)	92
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (—)	550
C_{13} 	 $Ph_2C{=}C{=}O$	C_6H_6	 (42) +  (38)	551
C_{14} 	MeCHClCOCl	Et_3N	 (63) +  (23)	552

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

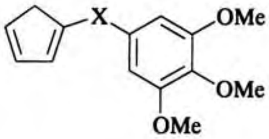
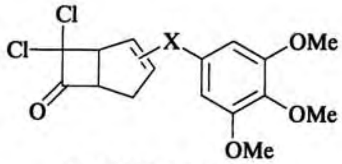
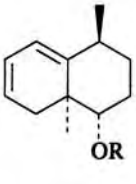
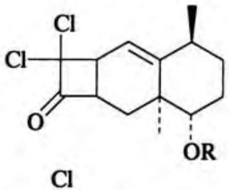
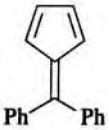
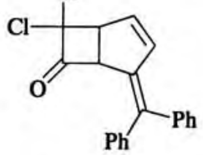
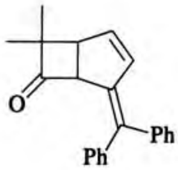
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 X = $CH_2C{\equiv}C$ (32) X = $CH_2CH{=}CH$ (—) X = $(CH_2)_3$ (42)	553
	$Cl_2CHCOCl$	Et_3N	 R = OTBDMS (—) R = OBn (—)	554 555
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (55)	502, 503
	i-PrCOCl	Et_3N, C_6H_{14}	 (32)	551

TABLE VI. [2+2] CYCLOADDITION OF KETENES TO CYCLIC DIENES (*Continued*)

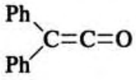
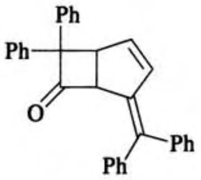
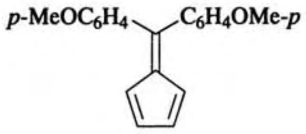
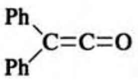
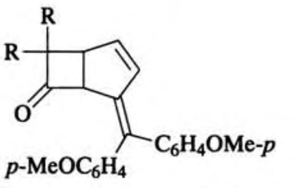
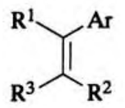
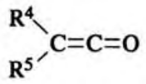
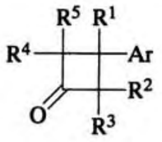
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	 $Ph_2C=C=O$	C_6H_6, rt, 2 d		(86)	551
	 $Ph_2C=C=O$	C_6H_{12}		R = Me (64) R = Ph, (91)	551

TABLE VII. [2+2] CYCLOADDITION OF KETENES TO ARENES

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		[a]		

Ar	R^1	R^2	R^3	R^4	R^5	Yield (%)	
p-ClC_6H_4	H	H	H	Ph	Ph	(82)	444
p-ClC_6H_4	H	H	H	Ph	Ph	(100)	556
Ph	H	D	D	Ph	Ph	(99)	50
Ph	D	H	H	Me	Me	(—)	557
Ph	D	H	H	Ph	Ph	(99)	50
Ph	D	H	H	Ph	Ph	(—)	51
Ph	H	D	H	t-Bu	CN	(—)	558
Ph	H	D	H	Ph	Ph	(—)	51
Ph	H	H	D	t-Bu	CN	(—)	558
Ph	H	H	H	Cl	Cl	(88)	83
Ph	H	H	H	Cl	Cl	(19)	403
Ph	H	H	H	Cl	Cl	(87)	298
Ph	H	H	H	Cl	CN	(86)	312
Ph	H	H	H	CF_3	CF_3	(80)	231
Ph	H	H	H	CF_3	CF_3	(—)	387
Ph	H	H	H	CF_3	CF_3	(80)	84
Ph	H	H	H	Me	Me	(20)	457
Ph	H	H	H	Me	Me	(40)	293
Ph	H	H	H	Ph	Ph	(93)	444
Ph	H	H	H	Ph	Ph	(100)	556
Ph	H	H	H	Ph	Ph	(94)	386
Ph	CD_3	H	H	Ph	Ph	(—)	21
p-$CF_3C_6H_4$	H	H	H	Ph	Ph	(100)	556

TABLE VII. [2+2] CYCLOADDITION OF KETENES TO ARENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.

Ar	R^1	R^2	R^3	R^4	R^5	Yield (%)	
Ph	Me	H	H	Ph	Ph	(98)	386
Ph	Me	H	H	Ph	Ph	(1)	559
Ph	Me	H	H	Ph	Ph	(98)	81
p-MeC_6H_4	H	H	H	Ph	Ph	(100)	556
p-MeC_6H_4	H	H	H	Ph	Ph	(81)	444
p-$MeOC_6H_4$	H	H	H	Ph	Ph	(84)	444
p-$MeOC_6H_4$	H	H	H	CF_3	CF_3	(79)	133
p-MeC_6H_4	Me	H	H	Cl	Cl	(84)	560
m-MeC_6H_4	Me	H	H	Me	Me	(—)	561

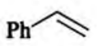
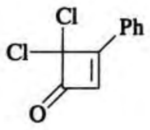
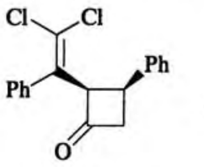
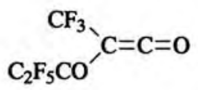
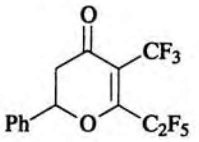
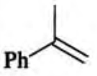
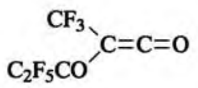
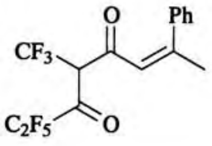
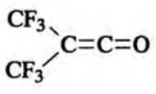
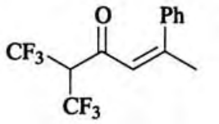
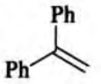
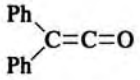
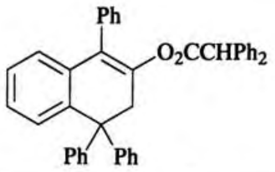
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		$h\nu$, C_6H_6	 (90)	306
	 $(CF_3)(C_2F_5CO)C{=}C{=}O$	Phenothiazine, 95°, 15 min	 (60)	346
C_9 	 $(CF_3)(C_2F_5CO)C{=}C{=}O$	95°, 60 h	 (59)	346

TABLE VII. [2+2] CYCLOADDITION OF KETENES TO ARENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Ref
	 $(CF_3)_2C{=}C{=}O$	100°, 2 h	 (96)	84
C_{14} 	 $Ph_2C{=}C{=}O$	150°, 3 d	 (58)	80, 444, 562

---

[a] The conditions were different for most entries and can be found by consulting the reference.

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES

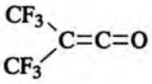
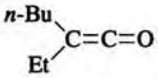
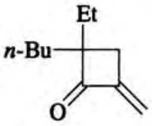
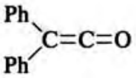
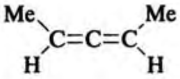
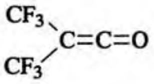
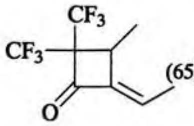
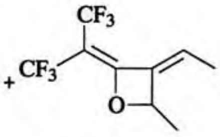
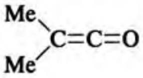
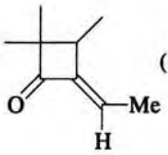
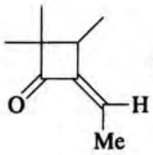
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
$CH_2{=}C{=}CH_2$	 $(CF_3)_2C{=}C{=}O$	165°	No reaction	336
	 $(n\text{-Bu})(Et)C{=}C{=}O$	—		563
	 $Ph_2C{=}C{=}O$	—	(—)	564
C_5				
 $MeHC{=}C{=}CHMe$	 $(CF_3)_2C{=}C{=}O$	100°, 60 h	 (65) +  (17)	336
	 $Me_2C{=}C{=}O$	130°, 2 h	 (17) +  (50)	93, 565-567

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

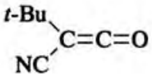
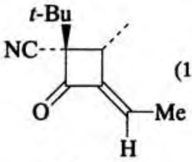
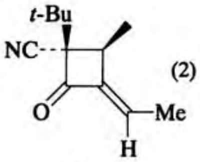
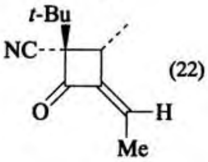
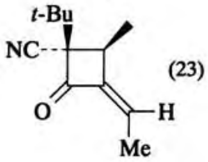
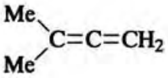
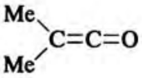
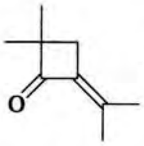
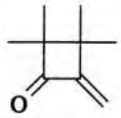
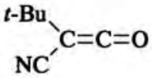
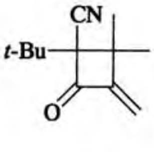
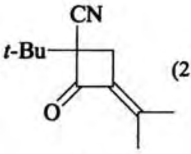
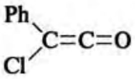
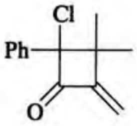
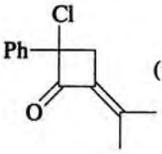
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(t\text{-Bu})(NC)C{=}C{=}O$	25°, 1 h	 (13) +  (2) +  (22) +  (23)	568, 94
 $Me_2C{=}C{=}CH_2$	 $Me_2C{=}C{=}O$	120°, 2 h	 (48) +  (20)	93, 569
	 $(t\text{-Bu})(NC)C{=}C{=}O$	0°, 1.5 h	 (41) +  (21)	568
	 $(Ph)(Cl)C{=}C{=}O$	—	 (4) +  (19)	564

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

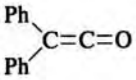
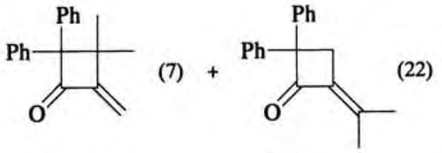
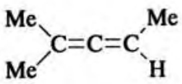
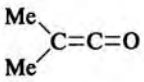
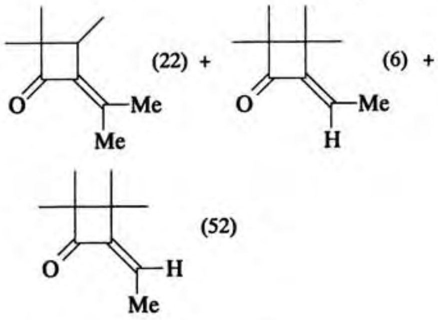
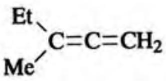
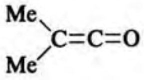
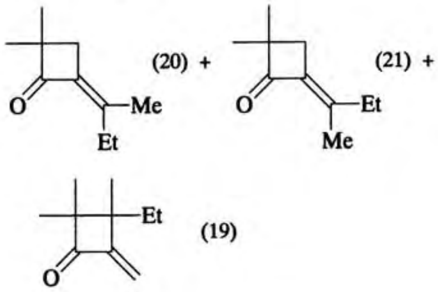
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	—	 (7) + (22)	564
C6				
 $Me_2C=C=CHMe$	 $Me_2C=C=O$	95°, 1 h	 (22) + (6) + (52)	93, 567
C7				
 $EtMeC=C=CH_2$	 $Me_2C=C=O$	120°, 2 h	 (20) + (21) + (19)	93, 569

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

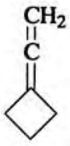
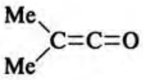
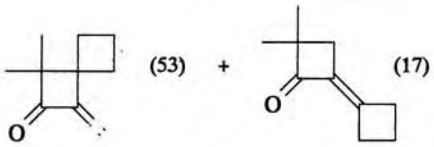
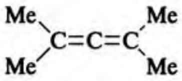
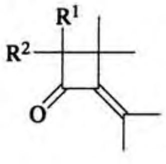
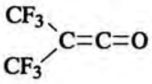
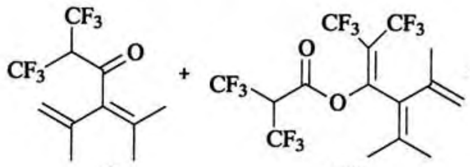
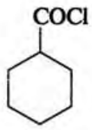
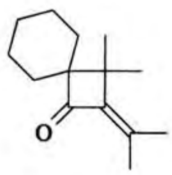
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C=C=O$	50°, 6 h	 (53) + (17)	93
 $Me_2C=C=CMe_2$	R¹R²CHCOCl	Et₃N, C₆H₁₄	 R¹ R² Yield (%) Me Cl (72) Me Br (65) Et Cl (70) Cl Cl (55) Cl Br (45) Cl H (25) Me H (20) Me Ph (90) Et Ph (90)	570
	 $(CF_3)_2C=C=O$	Et₂O	 (5) + (79)	336
		Et₃N, C₆H₆	 (60)	527

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

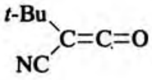
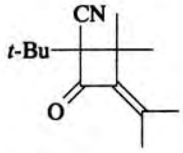
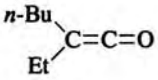
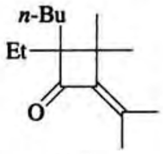
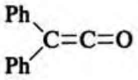
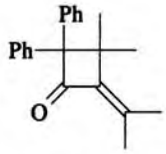
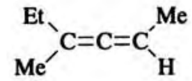
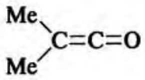
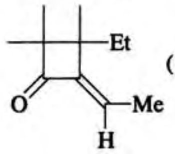
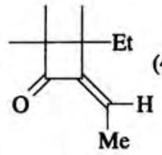
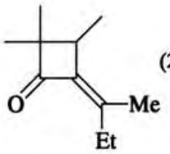
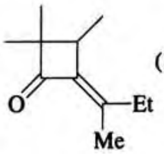
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $t\text{-Bu}(NC)C=C=O$	C_6H_6, 78°	 (77)	568
	 $n\text{-Bu}(Et)C=C=O$	rt, 4 h	 (48)	563
	 $Ph_2C=C=O$	rt, 4 h	 (—)	563
 $Et(Me)C=C=C(Me)H$	 $Me_2C=C=O$	95°, 1 h	 (10) +  (42) +  (2) +  (16)	93

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

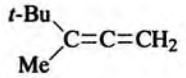
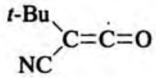
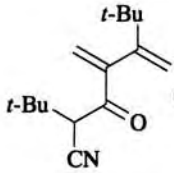
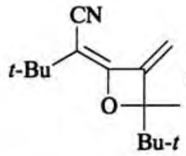
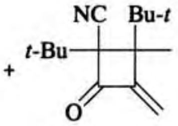
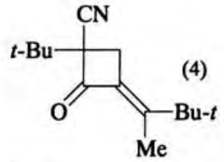
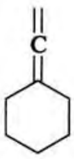
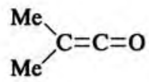
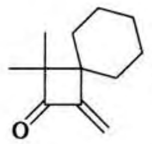
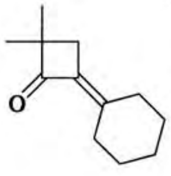
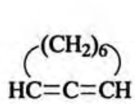
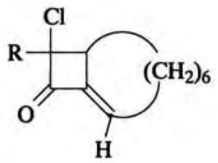
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
 $t\text{-Bu}(Me)C=C=CH_2$	 $t\text{-Bu}(NC)C=C=O$	C_6H_6, 78°	 (16) +  (1) +  (6) +  (4)	571
	 $Me_2C=C=O$	120°, 2 h	 (34) +  (36)	93, 569
C_9				
	RCHClCOCl	Et_3N, C_6H_{14}	 R = Cl (75) R = Me (72)	570

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

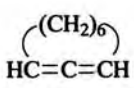
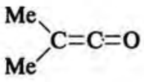
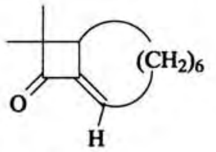
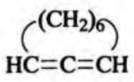
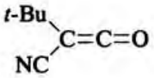
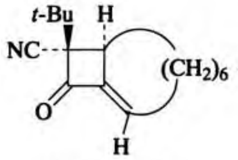
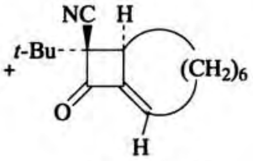
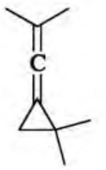
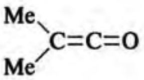
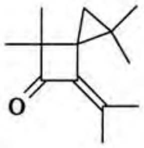
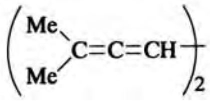
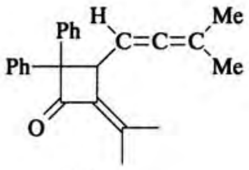
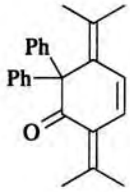
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
 $[\alpha]^{20}_{D}$ = -7.6°	 $Me_2C=C=O$	—	 (—) $[\alpha]^{20}_{D}$ = +2.2°	566, 572
 $[\alpha]^{25}_{D}$ = +20.43°	 $t\text{-}Bu(NC)C=C=O$	C_6H_6	 +  $[\alpha]^{25}_{D}$ = +29.68° $[\alpha]^{25}_{D}$ = -29.41°	573
	 $Me_2C=C=O$	50°, 6 h	 (100)	93, 423
C_{10}				
 $(Me_2C=C=CH-)_2$	$Ph_2CHCOCl$	Et_3N, C_6H_{14}	 (76) +  (<4)	574

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

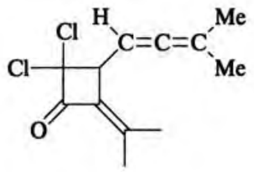
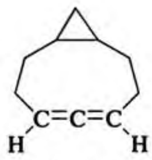
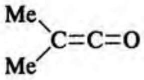
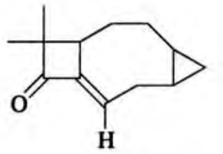
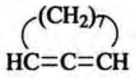
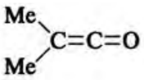
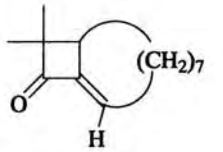
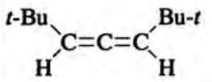
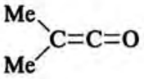
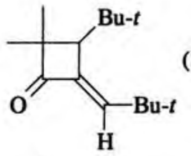
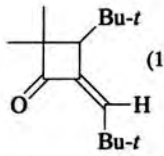
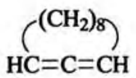
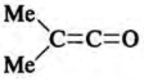
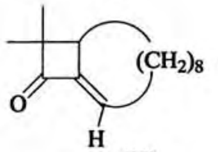
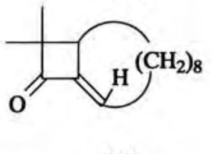
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (35)	574
 $[\alpha]^{21}_{D}$ = +22.4°	 $Me_2C=C=O$	80°	 (92) $[\alpha]^{23}_{D}$ = -6.5°	575, 566
	 $Me_2C=C=O$	50°, 6 h	 (100)	93
C_{11}				
	 $Me_2C=C=O$	125°, 2 h	 (15) +  (10)	93
	 $Me_2C=C=O$	120°, 4 h	 +  (32) (40)	93

TABLE VIII. [2+2] CYCLOADDITION OF KETENES TO ALLENES (*Continued*)

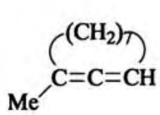
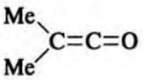
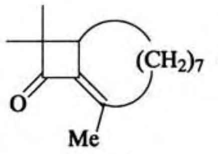
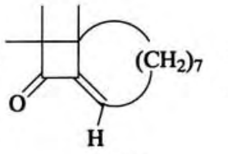
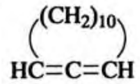
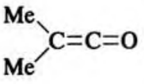
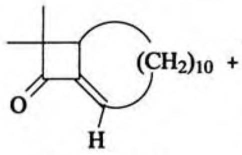
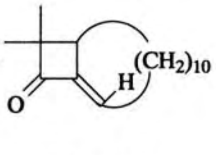
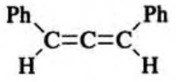
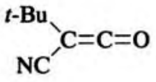
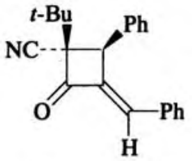
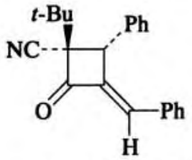
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C{=}C{=}O$	40°, 2 h	 (59) +  (26)	93, 570
C_{13}				
 $[\alpha]^{20}_D$ = +4.4°	 $Me_2C{=}C{=}O$	—	 $[\alpha]^{20}_D$ = -0.6° +  $[\alpha]^{20}_D$ = -0.7°	566
C_{15}				
 $[\alpha]_D$ = -365°	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, 78°	 (38) $[\alpha]_D$ = -21.4° +  (11) $[\alpha]_D$ = -213°	95

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES

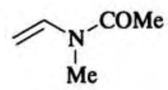
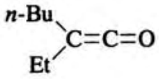
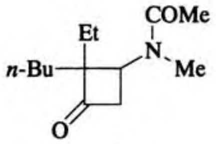
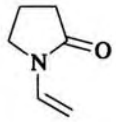
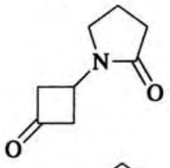
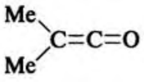
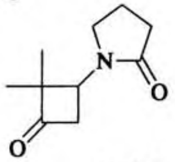
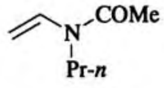
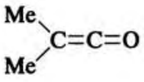
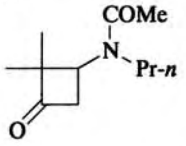
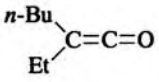
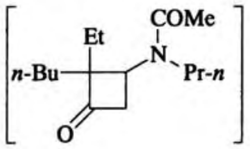
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
	 $(n\text{-Bu})(Et)C{=}C{=}O$	MeCN	 (62)	100
	$CH_2{=}C{=}O$	MeCN, reflux	 (—)	100
	 $Me_2C{=}C{=}O$	Et_2O, rt	 (30)	405, 100
	 $Me_2C{=}C{=}O$	Et_2O, rt	 (48)	405, 100
	 $(n\text{-Bu})(Et)C{=}C{=}O$	180°	 (—)	405

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

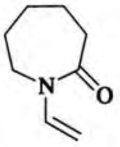
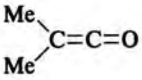
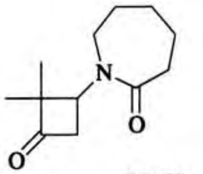
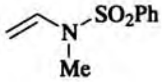
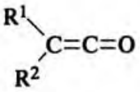
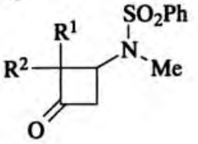
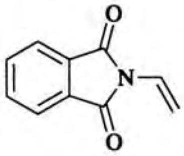
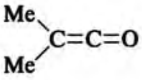
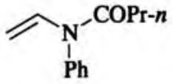
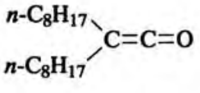
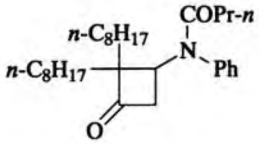
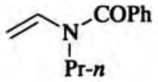
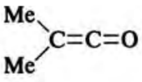
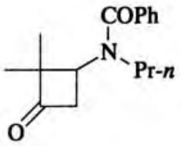
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C{=}C{=}O$	MeCN	 (—)	100
	 $R^1R^2C{=}C{=}O$	Et_2O, rt	 $R^1 = R^2 = Me$ (24) $R^1 = Et$, $R^2 =$ *i*-Bu (85)	405
	 $Me_2C{=}C{=}O$	Et_2O, rt	(—)	405
	 $(n\text{-}C_8H_{17})_2C{=}C{=}O$	MeCN, reflux	 (—)	100
	 $Me_2C{=}C{=}O$	C_6H_6	 (86)	405, 100

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

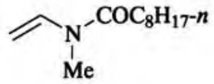
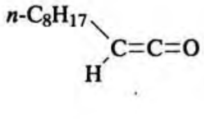
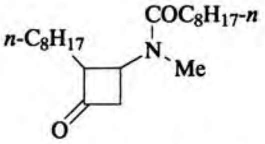
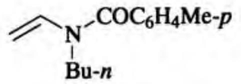
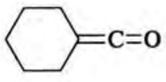
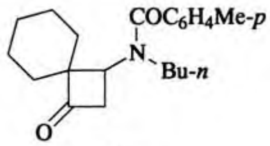
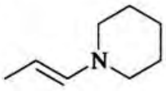
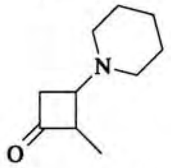
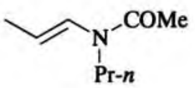
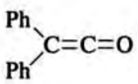
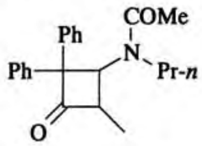
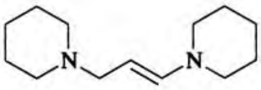
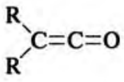
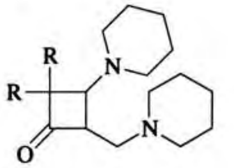
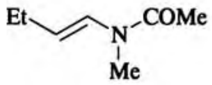
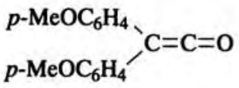
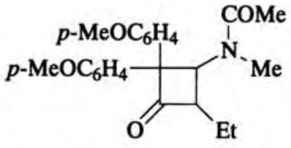
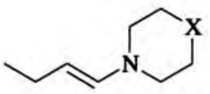
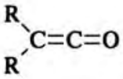
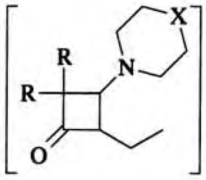
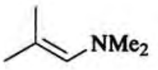
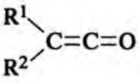
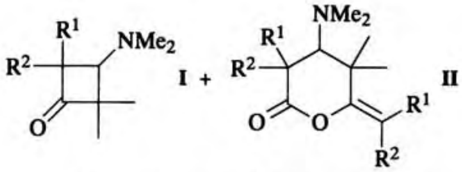
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $n\text{-}C_8H_{17}(H)C{=}C{=}O$	MeCN, reflux	 (—)	100
		MeCN, reflux	 (—)	100
C_3				
	$CH_2{=}C{=}O$	Et_2O, -40°	 (14)	576
	 $Ph_2C{=}C{=}O$	MeCN, reflux	 (99)	100, 405
	 $R_2C{=}C{=}O$	C_6H_{14}	 R = H (—) R = Me (—)	405

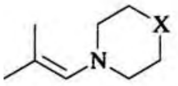
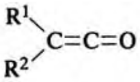
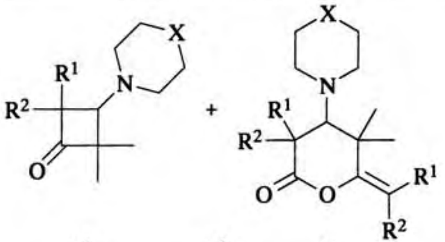
TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(p\text{-MeOC}_6\text{H}_4)_2\text{C=C=O}$	MeCN, reflux	 (—)	100
	 $\text{R}_2\text{C=C=O}$	*a*		
	 $\text{R}^1\text{R}^2\text{C=C=O}$	*a*		

R	X	Yield (%)	Refs.
H	O	(—)	98,577
H	CH_2	(—)	576
Me	CH_2	(—)	577

R^1	R^2	Yield I (%)	Yield II (%)	Refs.
H	H	(—)	(—)	577
Me	Me	(64)	(—)	578, 577
Me	Me	(—)	(32)	579
Et	Et	(—)	(12)	579, 578
Et	*n*-Bu	(—)	(—)	579, 578
Me	Et	(—)	(—)	578

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

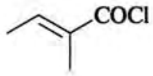
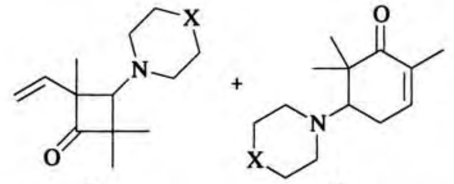
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $\text{R}^1\text{R}^2\text{C=C=O}$	*a*		

R^1	R^2	X	Refs.
H	H	—	576
Me	Me	—	580, 581
Me	H	—	582
Et	*n*-Bu	—	582
Br	CH_2=CH	—	97
Ph	Ph	—	99
H	H	O	576, 98
Me	H	O	582
Cl	H	O	582
PhO	H	O	582
MeO	H	O	582
Ph	H	O	582
Me	Me	O	582, 578, 64
Et	Et	O	582, 578
Ph	Ph	O	582, 580, 99
Me	Et	O	578
CH_2=CH	H	O	97
CH_2=C(Me)	H	O	97
CH_2=CH	Br	O	97
CH_2=C(Me)	Br	O	97
H	H	CH_2	576

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.

R^1	R^2	X	Refs.
Me	Me	CH_2	578-580, 583
Et	Et	CH_2	578
$-(CH_2)_5-$		CH_2	578
PhO	H	CH_2	582
i-Pr	H	CH_2	582
Bu	H	CH_2	582
n-$C_{16}H_{33}$	H	CH_2	582
Me	Me	NMe	578

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N	 I + II	97

X	Solvent	Temp.	Yield I (%)	Yield II (%)
—	CH_2Cl_2	rt	(0)	(53)
—	C_6H_{14}	70°	(28)	(28)
O	CH_2Cl_2	rt	(9)	(17)
O	C_6H_{14}	70°	(24)	(2)

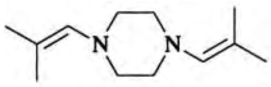
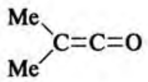
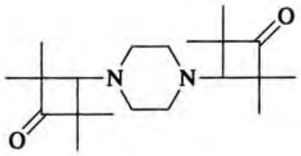
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C{=}C{=}O$	—	 (—)	578

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

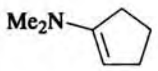
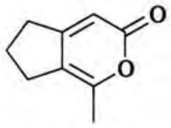
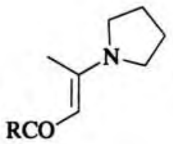
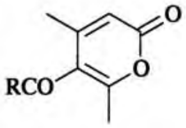
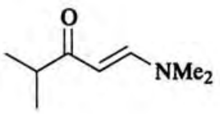
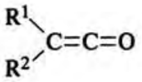
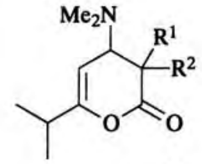
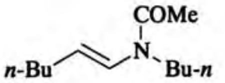
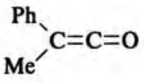
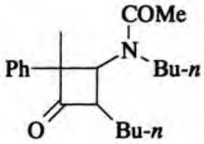
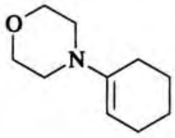
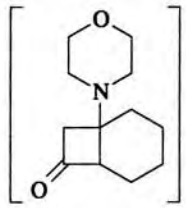
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
	$CH_2{=}C{=}O$	Et_2O, rt, 4 h	 (20)	98
C_6				
	$CH_2{=}C{=}O$	Et_2O, rt, 4 h	 R = Me (52) R = MeO (35)	98
	 $R^1R^2C{=}C{=}O$	C_6H_6, rt, 2 h	 $R^1 = R^2 =$ Me (86) $R^1 =$ Et, $R^2 =$ *n*-Bu (52)	584
	 Ph(Me)C=C=O	MeCN, reflux	 (—)	100
	$CH_2{=}C{=}O$	Et_2O, -40°, 2 h	 (—)	576, 585, 98

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

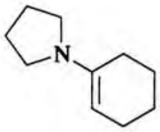
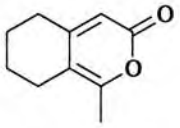
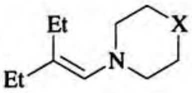
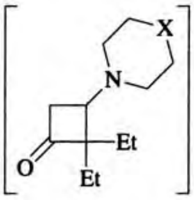
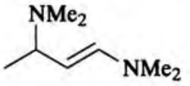
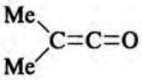
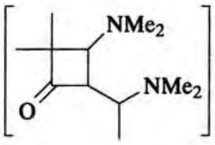
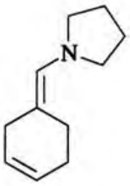
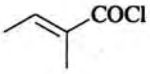
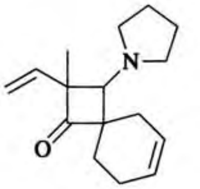
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	Et_2O, rt, 4 h	 (35)	98
	$CH_2{=}C{=}O$	Et_2O, -40°, 2 h	 (—) X = —, O, CH_2	576
	 $Me_2C{=}C{=}O$	C_6H_{14}	 (—)	405
C_7				
		Et_3N, CH_2Cl_2, rt	 (83)	97

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

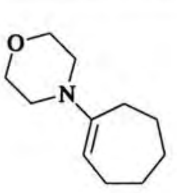
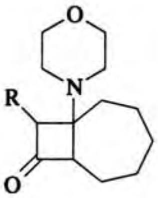
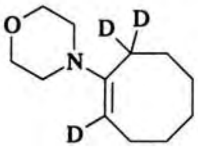
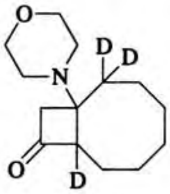
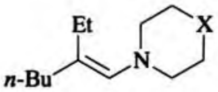
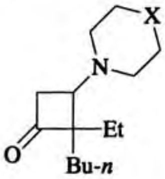
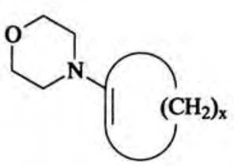
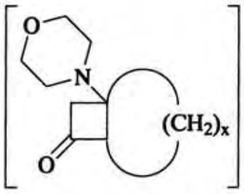
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Ref
	RCH_2COCl	Et_3N	 R = H (41) R = Me (29)	460
C_8				
	MeCOCl	Et_3N, Et_2O	 (—)	460, 586
	$CH_2{=}C{=}O$	Et_2O, -40°, 30 min	 (—) X = —, O, CH_2	576
C_9				
	MeCOCl	Et_3N, Et_2O	 (—) X = 7-11	586

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

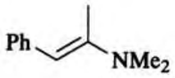
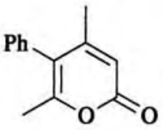
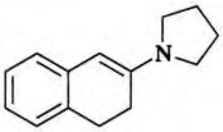
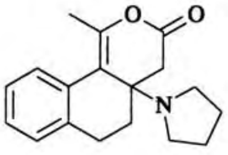
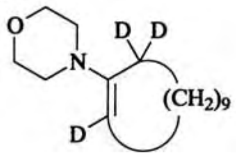
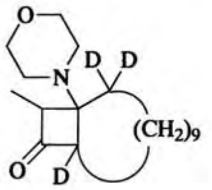
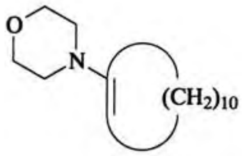
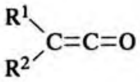
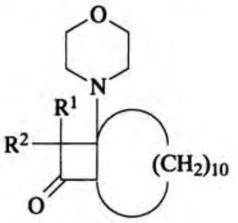
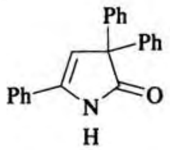
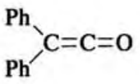
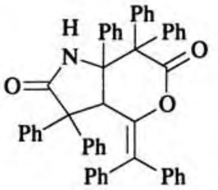
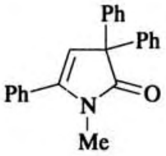
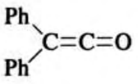
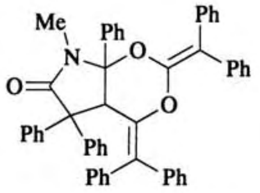
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$CH_2{=}C{=}O$	Et_2O, rt, 4 h		(34)	98
C_{10}					
	$CH_2{=}C{=}O$	Et_2O, rt, 4 h		(31)	98
C_{12}					
	EtCOCl	Et_3N, Et_2O		(—)	460

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	 $R^1R^2C{=}C{=}O$	*a*			
C_{22}					
	 $Ph_2C{=}C{=}O$	60°, 30 min		(—)	589

R^1	R^2	Yield (%)	
H	H	(39)	586, 587, 96, 588
Me	H	(31)	460, 96, 8
Me	Me	(0)	460
Me	Cl	(—)	460
n-Bu	H	(85)^b	96, 89
n-$C_{10}H_{21}$	H	(85)^b	96, 89
n-$C_{16}H_{33}$	H	(76)^b	96, 89
MeO_2CCH_2	H	(65)^b	96, 89
$EtO_2C(CH_2)_5$	H	(83)^b	96, 89

TABLE IX. [2+2] CYCLOADDITION OF KETENES TO ENAMINES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		rt, 5 d	 (—)	589

---

[a] The conditions were different for most entries and can be found by consulting the reference.

[b] The yield is of the 1,3-cyclotetradecanedione after hydrolysis.

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS

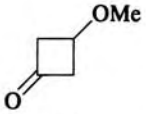
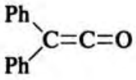
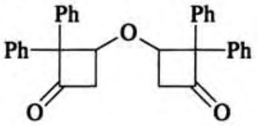
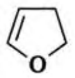
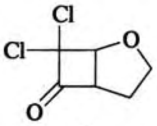
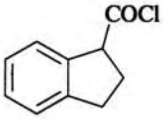
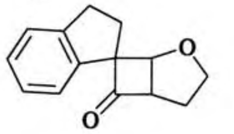
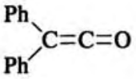
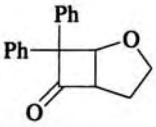
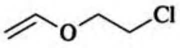
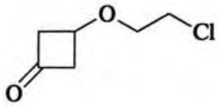
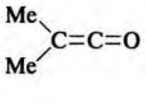
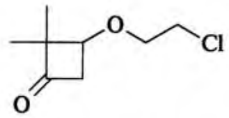
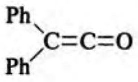
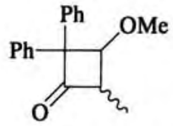
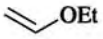
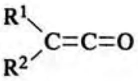
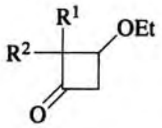
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
$CH_2=CHOMe$	$CH_2=C=O$	100°, 4 h	 (—)	590
C_4				
$(CH_2=CH)_2O$	 $Ph_2C=C=O$	C_6H_{14}, rt, 7 d	 (75)	591
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (56)	428
		Et_3N, Et_2O	 (89)	592
	 $Ph_2C=C=O$	0°	 (99)	103
	$CH_2=C=O$	MeCN, $ZnCl_2$, 50°	 (20)	101

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C{=}C{=}O$	rt	 (70)	321
	 $Ph_2C{=}C{=}O$	rt	 (—)	593
	 $R^1R^2C{=}C{=}O$	*a*		

R^1	R^2	Yield (%)	Refs.
Cl	Cl	(45)	403, 329
H	H	(30)	101, 590
Br	Me	(39)	442
Me	Me	(80)	321, 523
H	OEt	(85)	394, 101
H	$C(Me){=}CH_2$	(23)	343
H	CH_2OTMS	(60)	352
CN	*t*-Bu	(98)	55
Et	*n*-Bu	(81)	321
H	$PhC{=}CCl_2$	(80)	306
Ph	Ph	(82)	103, 591

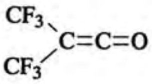
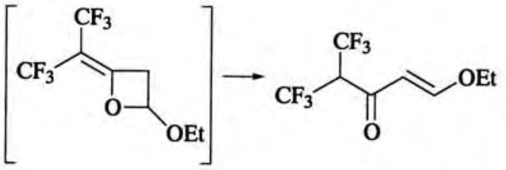
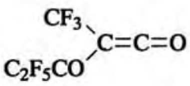
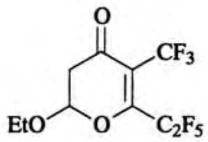
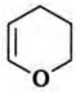
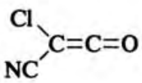
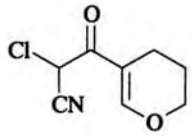
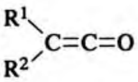
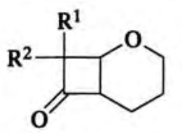
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(CF_3)_2C{=}C{=}O$	C_6H_{14}, rt, 16 h		133, 387, 231

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(CF_3)(C_2F_5CO)C{=}C{=}O$	Et_2O, 25°	 (75)	346
C_5 	 $Cl(NC)C{=}C{=}O$	PhMe, 103°	 (32)	312
	 $R^1R^2C{=}C{=}O$	*a*		

R^1	R^2	Yield (%)	Refs.
Cl	Cl	(35)	431, 441
H	H	(45)	101, 591
Br	Me	(50)	442
Cl	Me	(40)	442
Me	Me	(80)	321, 457
Me	OTMS	(—)	307
$-(CH_2)_5-$		(67)	527
H	$PhC{=}CCl_2$	(80)	306
Ph	Ph	(99)	103, 356
H	$(CH_2)_3C(Me){=}CH_2$	(50)	594

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

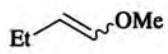
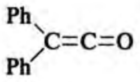
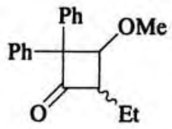
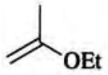
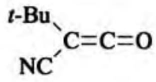
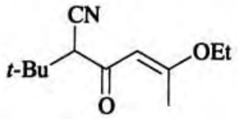
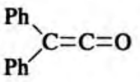
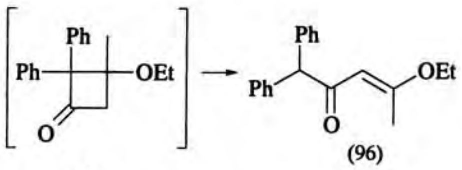
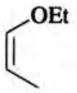
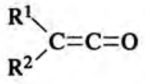
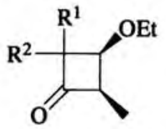
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		rt	 (—)	593
		C_6H_6, 78°	 (—)	55
		rt	 (96)	103
		*a*		
			R¹ R² Yield (%)	
			Me Me (64)	321
			Ph Me (100)	42
			Ph Et (100)	42
			Ph *n*-Pr (100)	42
			Ph *i*-Pr (100)	42
			Ph *t*-Bu (100)	42
			Ph Ph (—)	593,45

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

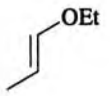
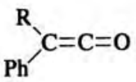
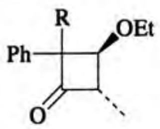
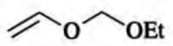
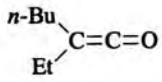
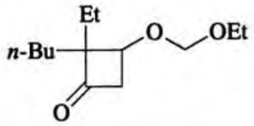
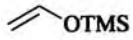
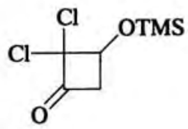
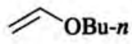
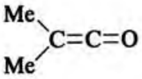
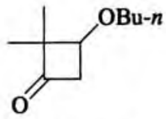
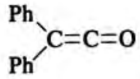
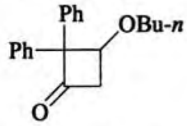
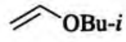
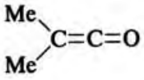
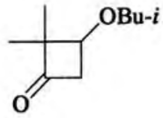
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		*a*		
			R Yield (%)	
			Me (100)	42
			Et (100)	42
			n-Pr (100)	42
			i-Pr (100)	42
			t-Bu (100)	42
			Ph (—)	45
		180°	 (34)	321
	Cl_3CCOCl	Zn, Et_2O	 (84)	104
C_6				
		rt	 (65)	321
		C_6H_6, rt, 3 h	 (99)	103
		rt	 (54)	321

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

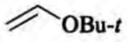
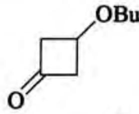
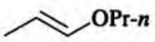
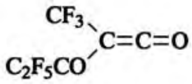
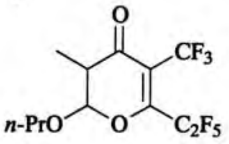
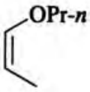
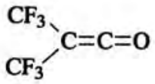
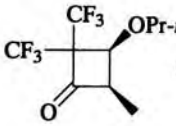
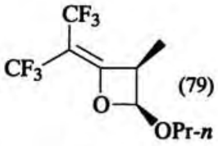
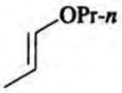
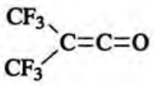
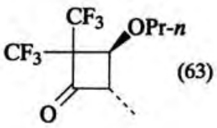
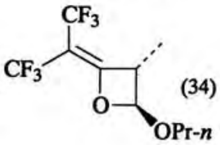
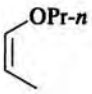
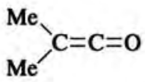
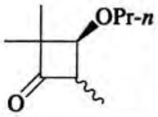
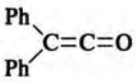
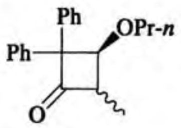
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Me_2CO	Ketene lamp	 (60)	595, 590
	 $(CF_3)(C_2F_5CO)C=C=O$	$CHCl_3$, 25°	 (65)	346
	 $(CF_3)_2C=C=O$	C_6H_{14}, -50°	 (20) +  (79)	133
	 $(CF_3)_2C=C=O$	0°, 2 h	 (63) +  (34)	133
	 $Me_2C=C=O$	Et_2O, rt, 1 h	 (89) *cis:trans* = 98.8:1.2	47, 395, 596
	 $Ph_2C=C=O$	Et_2O, rt, 1 h	 (99) *cis:trans* = 96.2:3.8	47, 395, 596

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

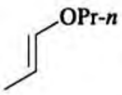
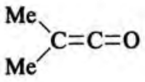
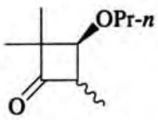
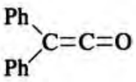
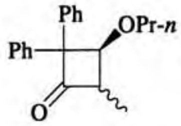
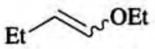
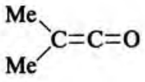
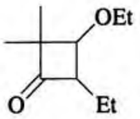
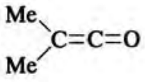
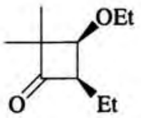
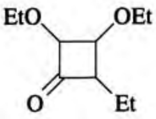
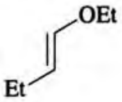
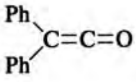
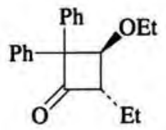
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C=C=O$	Et_2O, rt, 1 h	 (60) *cis:trans* = 0.8:99.2	47, 596, 395
	 $Ph_2C=C=O$	Et_2O, rt, 1 h	 (86) *cis:trans* = 2.5:97.5	47, 596, 597
 *cis:trans* = 3:97	 $Me_2C=C=O$	C_6H_6	 (43) *cis:trans* = 12:88	598
cis:trans = 88:12	 $Me_2C=C=O$	C_6H_6	 (69)	598
	$EtOCH_2COCl$	Et_3N	 (45)	101
	 $Ph_2C=C=O$	PhCN, 40°	 (—)	45, 593

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

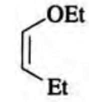
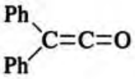
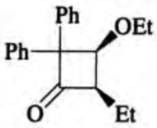
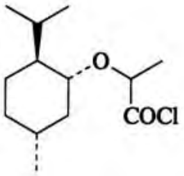
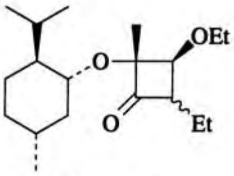
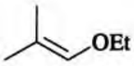
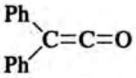
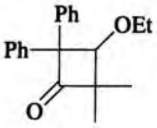
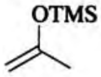
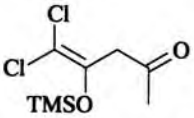
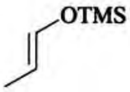
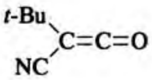
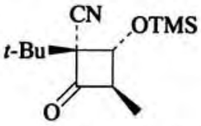
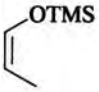
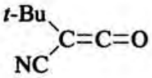
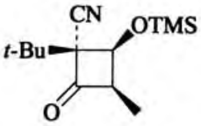
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	PhCN, 40°	 (—)	45, 593
		Et_3N, *t*-BuOMe	 (65) *cis:trans* =20:80	599
	 $Ph_2C=C=O$	MeCN, 1 min	 (43)	103, 45
	Cl_3CCOCl	Zn, Et_2O	 (79)	104
	 *t*-Bu(NC)C=C=O	C_6H_6, rt	 (97)	93
	 *t*-Bu(NC)C=C=O	C_6H_6, rt	 (95)	93

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

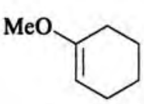
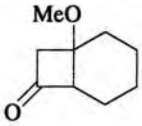
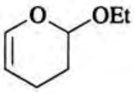
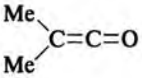
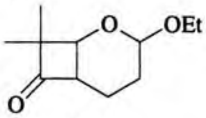
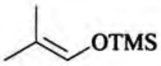
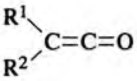
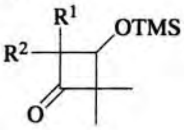
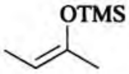
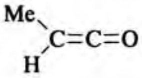
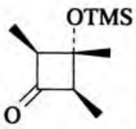
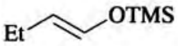
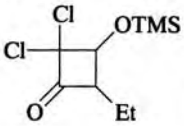
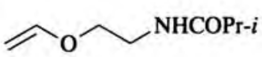
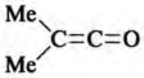
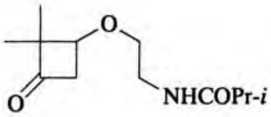
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	$CH_2=C=O$	MeCN, $ZnCl_2$, 60°	 (60)	101
	 $Me_2C=C=O$	rt	 (85)	321
	 $R^1R^2C=C=O$	*a*	 R^1 R^2 Yield (%) Cl Cl (92) Cl Me (61) Cl Ph (—) CN *t*-Bu (92)	 600, 104 104 104 40
	 MeHC=C=O	THF	 (44)	601
	Cl_3CCOCl	Zn, Et_2O	 (82)	104
C_8				
	 $Me_2C=C=O$	rt	 (80)	321

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

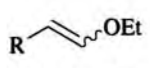
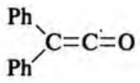
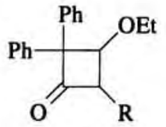
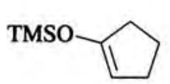
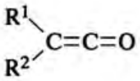
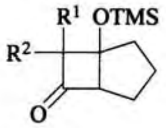
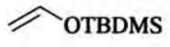
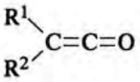
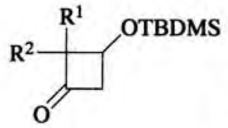
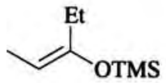
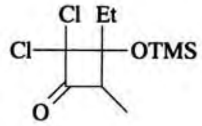
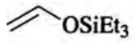
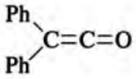
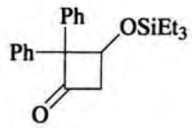
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = *i*-Pr, *t*-Bu	 $\mathrm{Ph(Ph)C{=}C{=}O}$	PhCN, 40°	 (—)	45
	 $\mathrm{R^1(R^2)C{=}C{=}O}$	*a*	 R^1 R^2 Yield (%) Cl Cl (77) Cl Me (79) Cl Ph (80) PhO Me (79) H PhO (68) H MeO (67) H Cl (53)	 104, 600 104, 416 104 104 104 104 104
	 $\mathrm{R^1(R^2)C{=}C{=}O}$	*a*	 R^1 R^2 Yield (%) Cl Me (80) Et Et (56) Ph Ph (86)	 602 102 102
	$\mathrm{Cl_3CCOCl}$	Zn, $\mathrm{Et_2O}$	 (80)	104
	 $\mathrm{Ph(Ph)C{=}C{=}O}$	—	 (100)	603

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

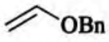
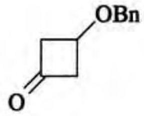
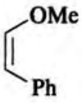
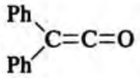
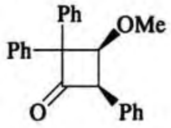
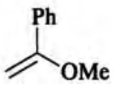
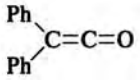
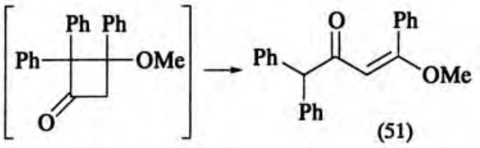
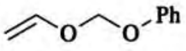
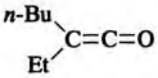
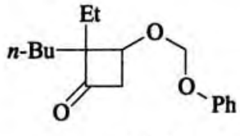
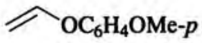
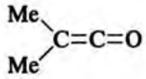
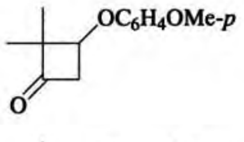
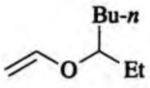
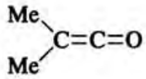
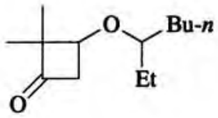
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	$\mathrm{CH_2{=}C{=}O}$	100°, 4 h	 (20)	590
	 $\mathrm{Ph(Ph)C{=}C{=}O}$	rt, 10 weeks	 (95)	103
	 $\mathrm{Ph(Ph)C{=}C{=}O}$	rt	 (51)	103
	 $\mathrm{n\text{-}Bu(Et)C{=}C{=}O}$	180°	 (45)	321
	 $\mathrm{Me(Me)C{=}C{=}O}$	rt	 (46)	321
	 $\mathrm{Me(Me)C{=}C{=}O}$	rt	 (56)	321

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

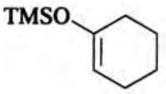
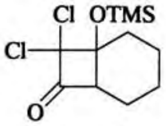
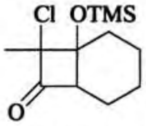
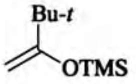
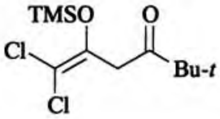
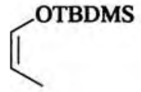
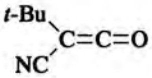
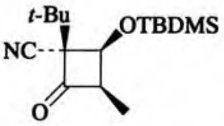
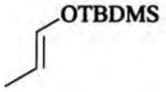
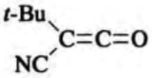
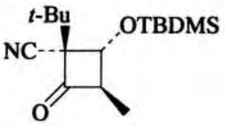
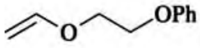
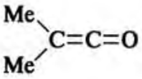
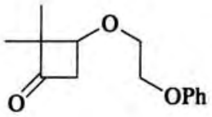
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn-Cu, Et_2O	 (81)	600
	MeCHClCOCl	Et_3N, C_6H_{14}	 (20)	416
	Cl_3CCOCl	Zn, Et_2O	 (82)	104, 600
	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, rt, 32 d	 (5)	40
	 $t\text{-Bu}(NC)C{=}C{=}O$	C_6H_6, 12 h	 (95)	40
	 $Me_2C{=}C{=}O$	rt	 (67)	321

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

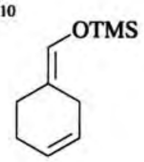
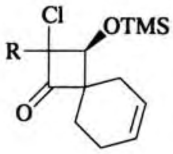
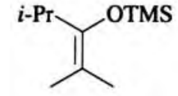
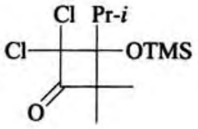
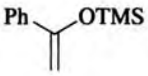
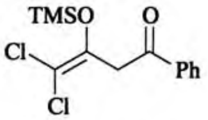
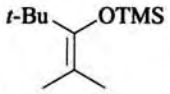
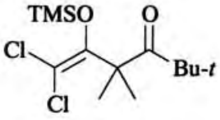
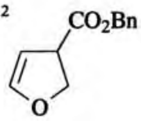
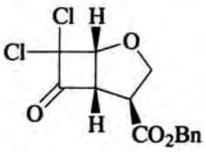
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	RCHClCOCl	Et_3N, C_6H_{14}	 R = Cl (70) R = Me (49) R = Ph (—)	104
	Cl_3CCOCl	Zn, Et_2O	 (88)	400
C_{11} 	Cl_3CCOCl	Zn-Cu, Et_2O	 (—)	600
	Cl_3CCOCl	Zn, Et_2O	 (66)	104
C_{12} 	$Cl_2CHCOCl$	Et_3N	 (59)	236

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

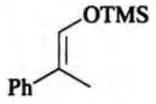
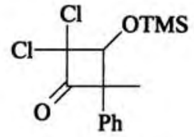
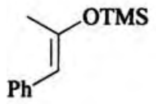
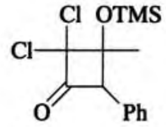
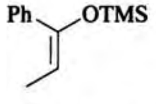
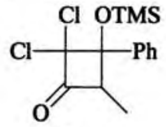
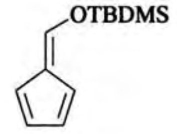
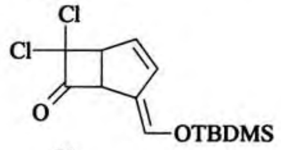
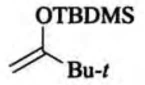
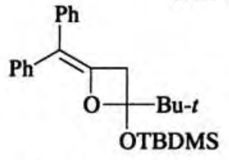
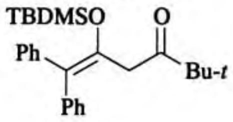
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn-Cu, Et_2O	 (86)	600, 104
	Cl_3CCOCl	Zn-Cu, Et_2O	 (59)	600
	Cl_3CCOCl	Zn-Cu, Et_2O	 (94)	600
	$Cl_2CHCOCl$	Et_3N, C_6H_{12}, rt	 (34)	604
	$Ph_2C{=}C{=}O$	rt	 (41) +  (45)	102

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

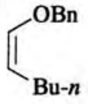
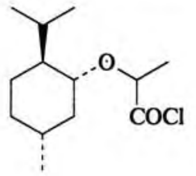
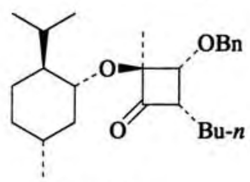
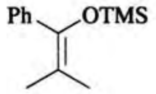
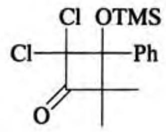
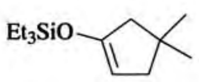
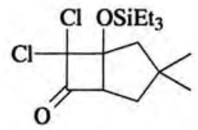
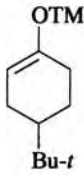
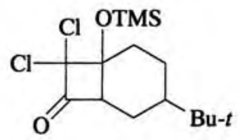
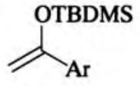
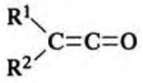
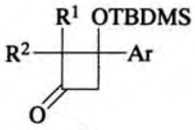
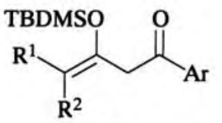
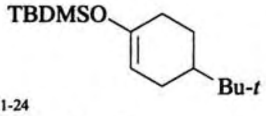
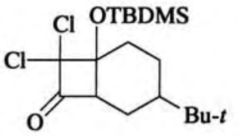
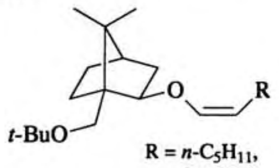
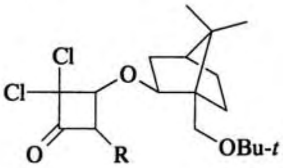
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 		Et_3N, t-BuOMe	 (50)	599
	Cl_3CCOCl	Zn, Et_2O	 (71)	104
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (83)	605, 606
	Cl_3CCOCl	Zn-Cu, Et_2O	 (95)	590

TABLE X. [2+2] CYCLOADDITION OF KETENES TO ENOL ETHERS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		[a]	 I  II	

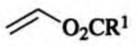
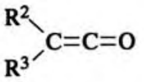
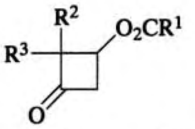
Ar	R^1	R^2	I	II	Refs.
p-$O_2NC_6H_4$	Cl	Cl	(—)	(—)	600
p-ClC_6H_4	Et	Et	I + II = (80)		102
p-$MeOC_6H_4$	Et	Et	I + II = (77)		102
Ph	Et	Et	I + II = (76)		102
p-ClC_6H_4	Ph	Ph	(—)	(99)	102
p-$MeOC_6H_4$	Ph	Ph	(—)	(6)	102
Ph	Ph	Ph	(—)	(76)	102

C_{16}				
	Cl_3CCOCl	Zn-Cu, Et_2O	 (92)	600
C_{21-24}				
 R = n-C_5H_{11}, $Ph(CH_2)_2$, n-C_8H_{17}	Cl_3CCOCl	Zn-Cu, Et_2O		

---

[a] The conditions for most entries are different, and can be found by consulting the reference.

TABLE XI. [2+2] CYCLOADDITION OF KETENES TO ENOL CARBOXYLATES

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $R^2R^3C=C=O$	a		

R¹	R²	R³	Yield (%)	
H	–(CH₂)₆–		(—)	608
CCl_3	Me	Me	(31)	608
Me	CN	*t*-Bu	(97)	55
Me	Et	*n*-Bu	(36)	608,321
Me	Et	*s*-Bu	(34)	321
Me	Et	*i*-Bu	(30)	608
Me	Ph	Ph	(72)	608,321
CH=CHMe	Me	Ph	(—)	608
CH_2=CMe	Ph	Ph	(72)	608
t-Bu	H	H	(—)	608
Ph	Ph	Ph	(44)	608
$C_{11}H_{23}$	Ph	Ph	(—)	608

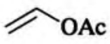
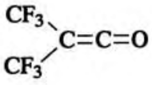
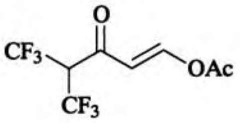
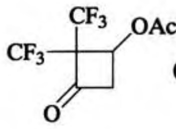
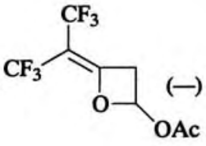
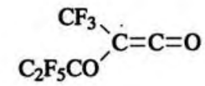
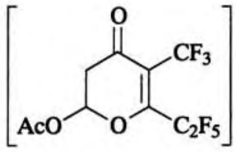
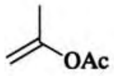
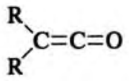
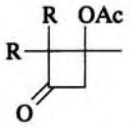
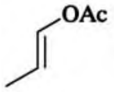
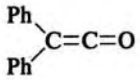
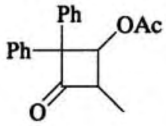
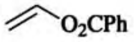
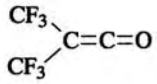
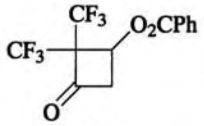
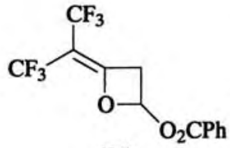
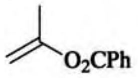
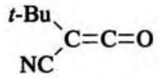
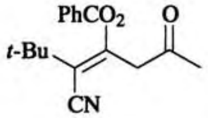
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 	 $(CF_3)_2C=C=O$	100°	 (40) +  (—) +  (—)	133

TABLE XI. [2+2] CYCLOADDITION OF KETENES TO ENOL CARBOXYLATES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Phenothiazine, 95°, 15 min	 (—)	346
		rt, 2 d	 R = Ph (—) R = n-C_8H_{17} (—) R = CN, t-Bu (—)	608
		rt, 2 d	 (—)	608
C_9 		100°, 16 h	 (42) +  (34)	133, 609
C_{10} 		C_6H_6, 78°	 (—)	55

[a] The conditions for most entries are different and can be found by consulting the reference.

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS

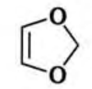
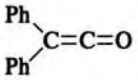
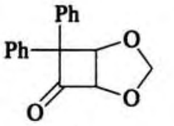
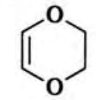
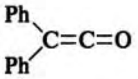
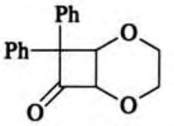
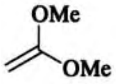
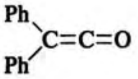
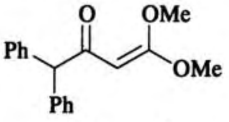
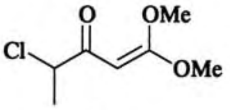
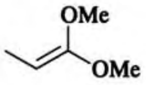
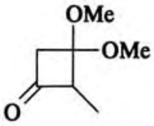
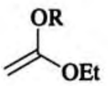
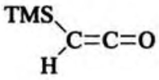
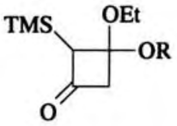
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 $Ph_2C=C=O$	MeCN, rt, 6 d	 (52)	103
C_4				
	 $Ph_2C=C=O$	45 d	 (80)	103
	 $Ph_2C=C=O$	80°, 30 min	 (57)	610
	MeCHClCOCl	Et_3N	 (85)	611
C_5				
	$CH_2=C=O$	MeCN, $ZnCl_2$, 25°	 (35)	101
	 $TMS(H)C=C=O$	90°, 2 h	 R = Me, Et (50)	612

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

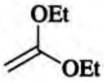
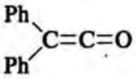
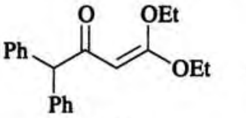
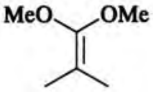
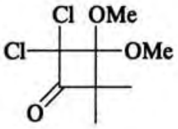
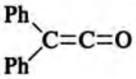
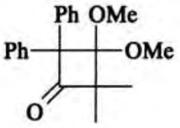
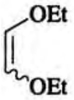
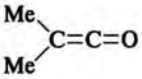
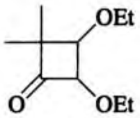
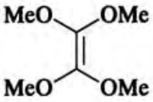
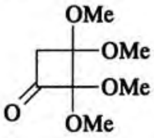
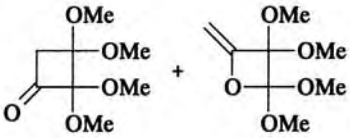
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	 $Ph_2C=C=O$	C_5H_{12}, -50°	 (99)	103
	$Cl_2CHCOCl$	Et_3N	 (82)	611
	 $Ph_2C=C=O$	100°	 (36)	105
	 $Me_2C=C=O$	rt	 (20)	321
	$CH_2=C=O$	MeCN, $ZnCl_2$, rt	 (40)	101
	$CH_2=C=O$	rt, 4 h	 (total 72)	106, 613

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

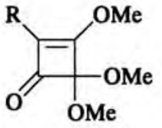
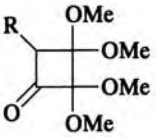
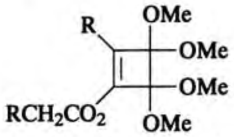
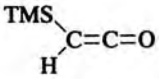
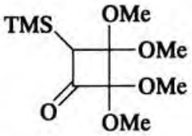
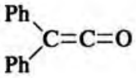
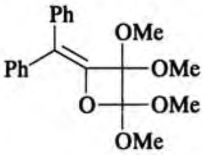
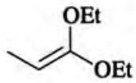
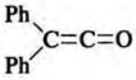
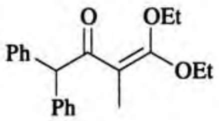
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCH_2COCl	Et_3N, C_6H_{14}	 I +  II +  III R = *t*-Bu, I + II + III (83) R = CH_2CO_2Me, I + II + III (34)	614
	 $TMS(H)C=C=O$	90°, 2 h	 (65)	615
	 $Ph_2C=C=O$	Dioxane, 60-70°	 (45)	106
C_7				
	 $Ph_2C=C=O$	80°, 30 min	 (72)	610

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

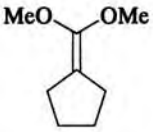
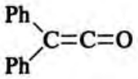
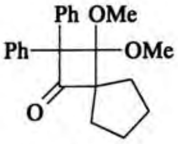
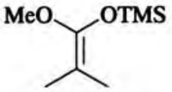
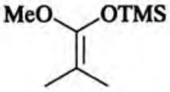
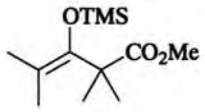
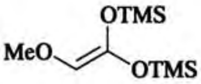
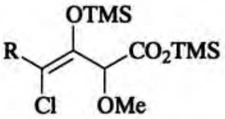
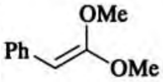
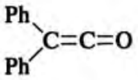
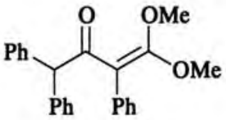
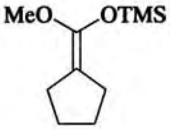
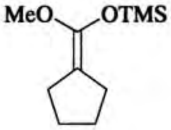
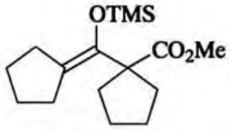
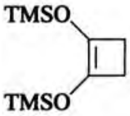
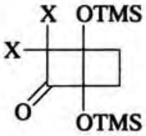
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$				
	 $Ph_2C=C=O$	100°, 12 h	 (35)	105
		200°, 4 h	 (75)	308
C$_9$				
	RCHClCOCl	Et$_3$N, C$_6$H$_{14}$	 R = H (80) R = Cl (87) R = Me (85) *cis:trans* = 1:1	611
C$_{10}$				
	 $Ph_2C=C=O$	90-95°, 7 h	 (40)	616, 610
		200°, 4 h	 (75)	308
	X$_3$CCOCl	Zn, Et$_2$O	 X = F (34) X = Cl (55) X = Br (45)	617

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

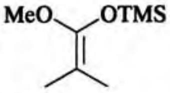
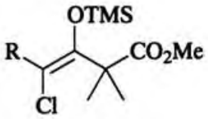
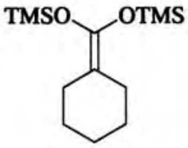
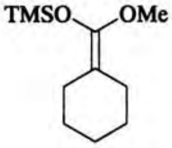
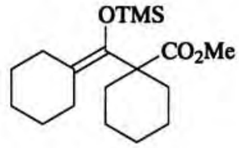
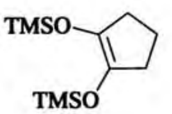
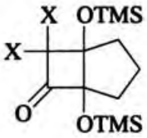
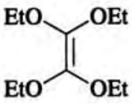
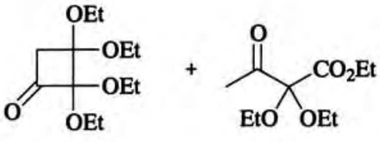
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCHClCOCl	Et$_3$N, C$_6$H$_{14}$	 R = H (80) R = Cl (80) R = Me (82)	611
C$_{11}$				
		200°, 4 h	 (75)	308
	X$_3$CCOCl	Zn, Et$_2$O	 X = F (47) X = Cl (75) X = Br (74)	617
	CH$_2$=C=O	0-5°, 14 h	 (88) (6)	613

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

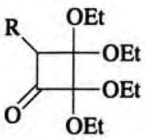
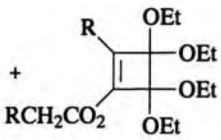
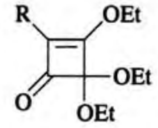
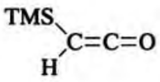
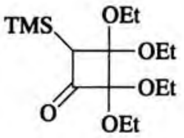
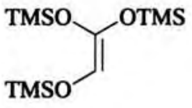
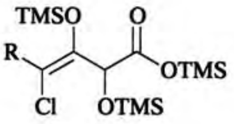
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	RCH_2COCl	Et_3N, C_6H_{14}	 I +  II +  III R I + II + III Me (55) *t*-Bu (81) *n*-C_6H_{13} (78) C_6H_{11} (75) Bn (85) Cl_2C=CH (62) Ph (60) *p*-$MeOC_6H_4$ (78) *p*-ClC_6H_4 (71)	614
		90°, 2 h	 (68)	615
	RCHClCOCl	Et_3N, C_6H_{14}	 R = H (80) R = Cl (85) R = Me (85)	611

TABLE XII. [2+2] CYCLOADDITION OF KETENES TO POLYOXYGENATED OLEFINS (*Continued*)

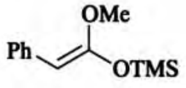
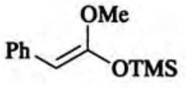
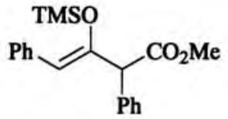
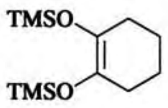
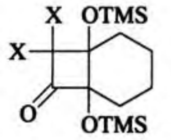
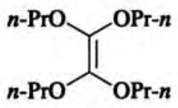
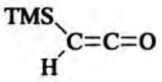
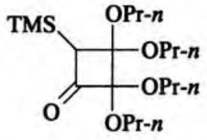
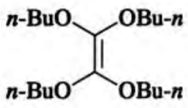
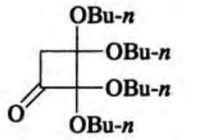
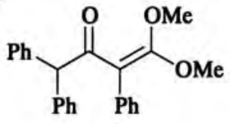
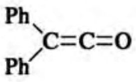
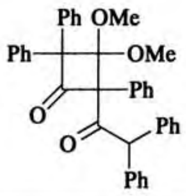
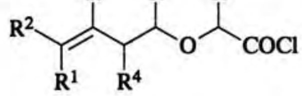
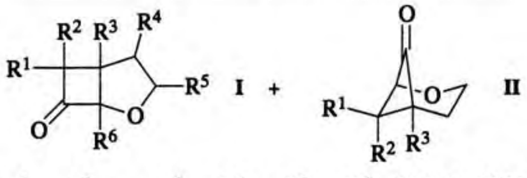
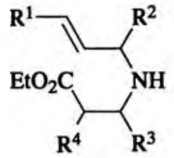
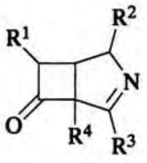
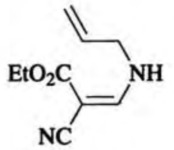
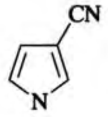
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		200°, 4 h	 (85)	308
	X_3CCOCl	Zn, Et_2O	 X = F (55) X = Cl (65) X = Br (82)	617
C_{14} 		—	 (—)	615
C_{18} 	CH_2=C=O	0-5°, 14 h	 (83)	613
C_{24} 		80-85°, 1 h	 (—)	616

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS

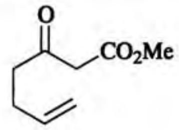
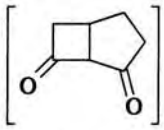
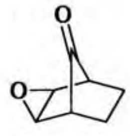
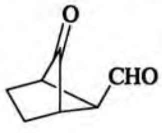
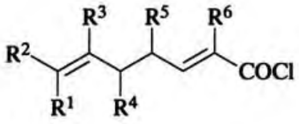
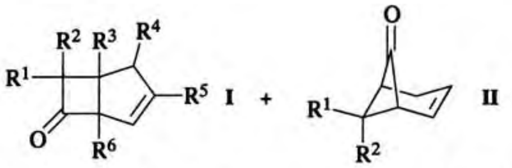
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	Et_3N, C_6H_6, reflux		

R^1	R^2	R^3	R^4	R^5	R^6	Yield I	Yield II	Refs.
H	H	H	H	H	H	(16)	(0)	618, 619
H	H	Me	H	H	H	(72)	(0)	618, 619
Me	Me	H	H	H	H	(0)	(52)	618, 619
H	H	Me	H	H	Me	(50)	(0)	620
H	H	Me	H	Me	H	(73)	(0)	620, 619
H	H	Me	Me	H	H	(63)	(0)	620, 619
H	Et	H	H	H	H	(47)	(19)	619
H	–(CH$_2$)$_4$–		H	H	H	(58)	(5)	620

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	400°		
	400°	 (30)	302

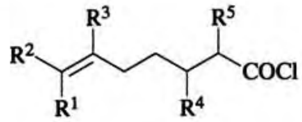
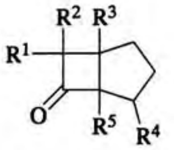
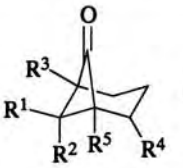
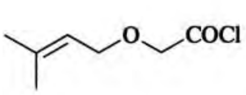
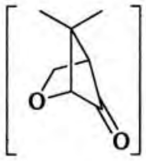
R^1	R^2	R^3	R^4	Yield	Refs.
H	H	Me	H	(46)	302, 621
H	H	Me	Me	(62)	302
H	Me$_2$	H	H	(67)	302
Me	H	Me	Me	(46)	302
H	H	Ph	H	(45)	621
H	H	Me	Ph	(60)	302
H	H	–(CH$_2$)$_3$–		(32)	302
H	H	–(CH$_2$)$_4$–		(33)	302

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	550°, 10^{-2} torr	 (—)	622, 623
	*hv*, C_6H_6	 (—)	624
	Et_3N, PhMe, reflux		

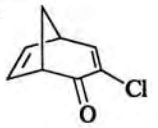
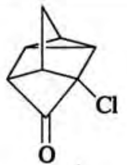
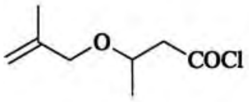
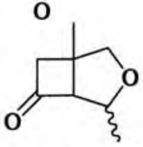
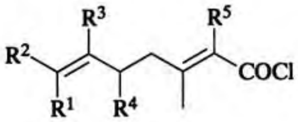
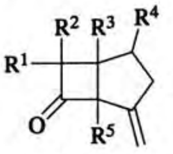
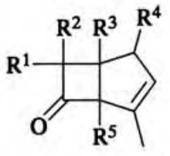
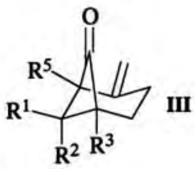
R^1	R^2	R^3	R^4	R^5	R^6	Yield I	Yield II	Refs.
H	H	H	H	H	H	(48)	(0)	625, 107
H	H	H	H	H	Me	(48)	(0)	107
H	Me	H	H	H	H	(38)	(9)	107
Me	Me	H	H	H	H	(0)	(41)	107
Et	H	H	H	H	H	(46)	(5)	625, 107
H	H	H	H	CH$_2$CH=CH$_2$	H	(83)	(0)	626
H	H	Me	H	CH$_2$C(Me)=CH$_2$	H	(84)	(0)	626
H	H	H	CH$_2$OTBDPS	H	H	(39)	(0)	107
H	H	H	CH$_2$OMe	H	H	(40)	(0)	107

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et$_3$N, C$_6$H$_6$, reflux	 I +  II	
	Et$_3$N, C$_6$H$_6$	 (—)	620

R^1	R^2	R^3	R^4	R^5	Yield I	Yield II	Refs.
H	H	H	H	Cl	(68)	(0)	627
H	H	H	H	H	(9)	(0)	626
H	H	Me	H	H	(—)	(0)	628, 594, 626
H	H	Ph	H	H	(—)	(0)	628, 594
H	H	H	H	CH=CH$_2$	(51)	(0)	625
H	–(CH$_2$)$_3$–		H	H	(50)	(0)	107, 629
H	–(CH$_2$)$_3$–		H	Me	(45)	(0)	630
H	Et	H	H	H	(26)	(14)	627
Me	Me	H	Me	Cl	(0)	(55)	627
H	H	H	H	3-furyl	(71)	(0)	631
H	H	H	H	Ph	(74)	(0)	631
H	H	H	H	1-cyclohexenyl	(68)	(0)	631
H	H	H	H	2-naphthyl	(88)	(0)	631

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$ 	*h*ν, Et$_2$O	 (—)	632
	Et$_3$N, CH$_2$Cl$_2$	 (70)	633
	Et$_3$N, PhMe	 I  II  III	

R^1	R^2	R^3	R^4	R^5	Yield I	Yield II	Yield III	Refs.
H	H	H	H	H	(41)	(0)	(0)	625
H	H	H	H	H	(48)	(12)	(0)	110
H	H	Me	H	H	(43)	(0)	(0)	625, 107, 110
Me	Me	H	H	H	(0)	(0)	(45)	109, 107, 634-636
CH$_2$OMe	Me	H	H	H	(0)	(0)	(30)	109
H	H	H	H	Me	(27)	(0)	(9)	637
H	H	H	H	CH$_2$C≡CEt	(38)	(0)	(7)	637
H	H	H	Me	H	(39)	(0)	(0)	110, 107
Me$_2$C=CH(CH$_2$)$_2$	Me	H	H	H	(0)	(0)	(43)	638, 109
Me	Me$_2$C=CH(CH$_2$)$_2$	H	H	H	(0)	(0)	(39)	109
EtCH=CH(CH$_2$)$_7$	Me	H	H	H	(0)	(0)	(30)	634
Me	EtCH=CH(CH$_2$)$_7$	H	H	H	(0)	(0)	(38)	634

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

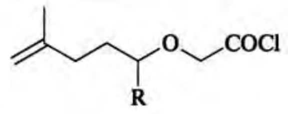
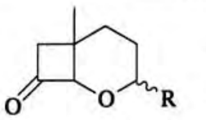
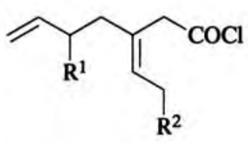
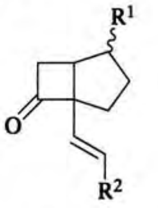
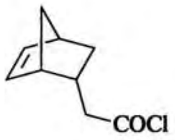
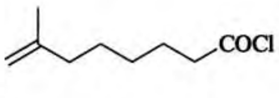
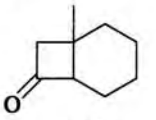
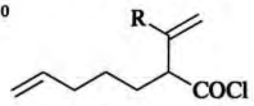
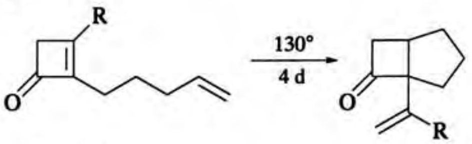
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et$_3$N, C$_6$H$_6$, reflux	 R = H (62) R = Me (58)	620, 619
C$_9$			
	Et$_3$N, PhMe, reflux	 R^1 = H, R^2 = H (50) R^1 = Me, R^2 = H (52) R^1 = H, R^2 = Et (52)	108
	Et$_3$N, C$_6$H$_6$, reflux	 (61)	639
	Et$_3$N	 (3)	626
C$_{10}$			
	Et$_3$N, PhMe, reflux	 R = Me (56) R = Et (87) R = Me (76) R = Et (75)	108

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

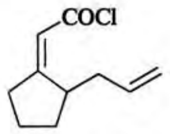
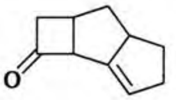
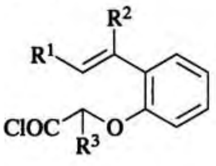
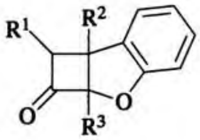
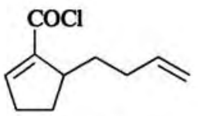
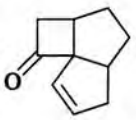
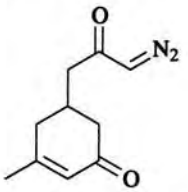
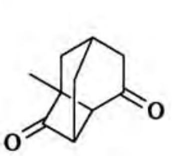
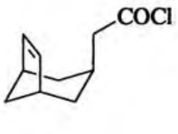
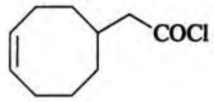
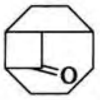
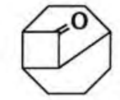
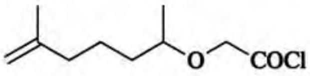
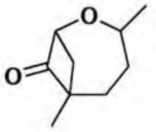
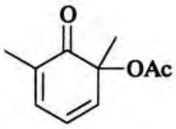
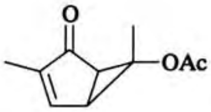
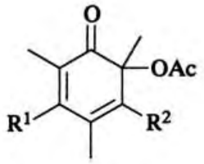
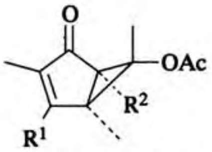
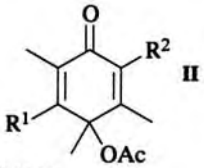
<table>
<tr><th>Reactant</th><th>Conditions</th><th colspan="5">Product(s) and Yield(s) (%)</th><th>Refs.</th></tr>
<tr><td> </td><td>Et$_3$N</td><td colspan="5"> (62)</td><td>640</td></tr>
<tr><td rowspan="9"> </td><td rowspan="9">Et$_3$N, C$_6$H$_6$, reflux</td><td rowspan="9"> </td><td>R^1</td><td>R^2</td><td>R^3</td><td>Yield</td><td></td></tr>
<tr><td>H</td><td>H</td><td>H</td><td>(70)</td><td>619, 620</td></tr>
<tr><td>Me</td><td>H</td><td>H</td><td>(72)</td><td>618</td></tr>
<tr><td>H</td><td>H</td><td>Me</td><td>(60)</td><td>618</td></tr>
<tr><td>Me</td><td>H</td><td>Me</td><td>(76)</td><td>618</td></tr>
<tr><td>Me</td><td>H</td><td>Et</td><td>(71)</td><td>618</td></tr>
<tr><td>H</td><td>Ph</td><td>H</td><td>(88)</td><td>618</td></tr>
<tr><td>Me</td><td>H</td><td>Ph</td><td>(85)</td><td>618, 322</td></tr>
<tr><td>H</td><td>Ph</td><td>Me</td><td>(84)</td><td>618</td></tr>
<tr><td> </td><td>*i*-Pr$_2$NEt, DMAP, PhMe, reflux</td><td colspan="5"> (78)</td><td>629</td></tr>
<tr><td> </td><td>*h*ν, C$_6$H$_6$</td><td colspan="5"> (24)</td><td>641</td></tr>
<tr><td> </td><td>Et$_3$N</td><td colspan="5"> (54-76)</td><td>642</td></tr>
</table>

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCHCl_2$, reflux or Et_3N	 (1) +  (10)	643
	Et_3N, C_6H_6, reflux	 (30)	619, 620
	*hv*	 (36-43)	644
	*hv*	 I +  II	644

R^1	R^2	Yield I	Yield II
H	H	(45)	(27)
Me	H	(57)	(45)
Me	Me	(42)	(30)

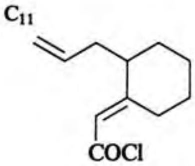
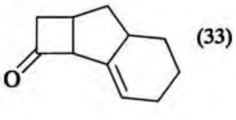
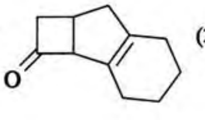
	Et_3N, PhMe, reflux	 (33) +  (25)	110

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

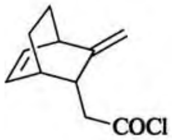
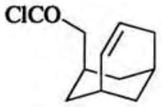
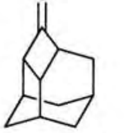
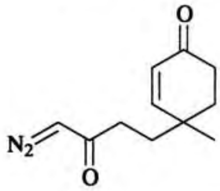
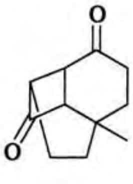
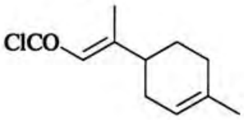
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N, C_6H_6, reflux	 (44)	645
	Et_3N, C_6H_6, reflux	 (46)	646
	*hv*, C_6H_{12}, dioxane	 (32)	315, 641
	Et_3N, PhMe, reflux	 (59)	647

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

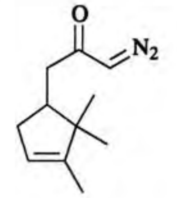
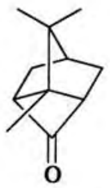
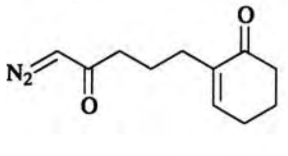
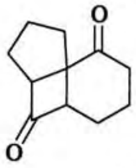
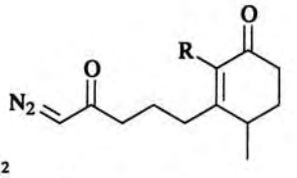
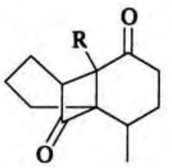
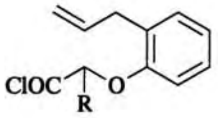
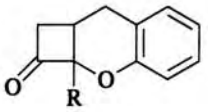
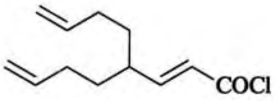
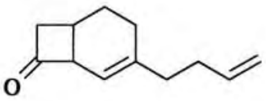
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	hν, C_5H_{12}	 (79)	648
	hν, C_6H_{12}, dioxane	 (39)	315
	hν, C_6H_{12}, dioxane	 R = H (34) R = Me (30)	315, 649
C_{12}			
	Et_3N, C_6H_6, reflux	 R = Me (43) R = Et (49)	618, 322
	Et_3N	 (8)	626

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

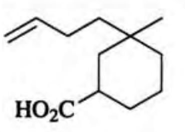
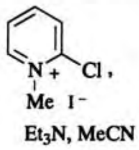
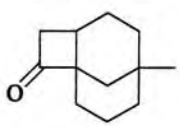
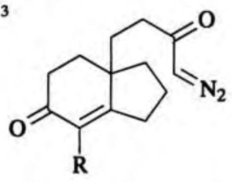
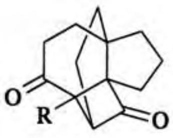
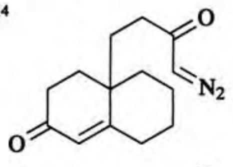
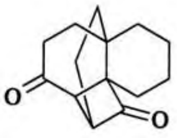
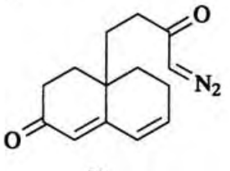
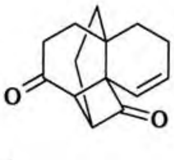
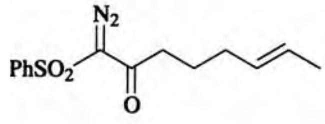
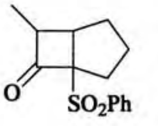
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	 Et_3N, MeCN	 (47)	650
C_{13}			
	hν, C_6H_{12}, dioxane	 R = H (30) R = Me (30)	315
C_{14}			
	hν, C_6H_6, dioxane	 (40)	641, 649
	hν, C_6H_{12}, dioxane	 (29)	315
	174°, n-$C_{10}H_{21}$	 (31)	651

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

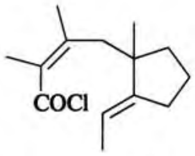
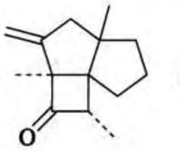
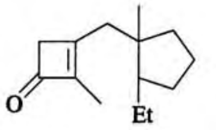
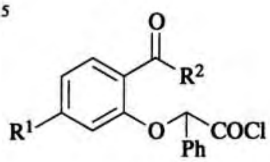
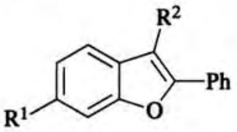
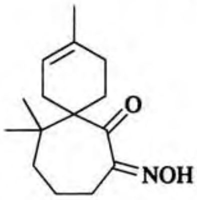
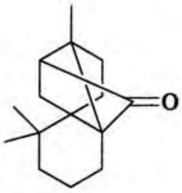
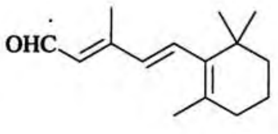
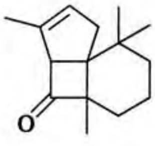
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Et_3N, PhMe, reflux	 (31) +  (6)	647
C_{15}			
	Et_3N	 $R^1 = R^2 = H$ (75) R^1 = MeO, R^2 = Ph (82)	322
	1. NH_2Cl, THF 2. *hν*, Et_2O	 (90)	652
	Distill in vacuo	 (50)	653

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

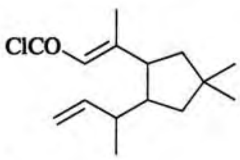
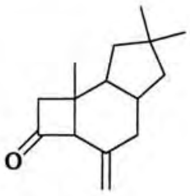
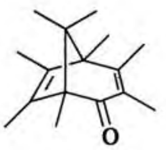
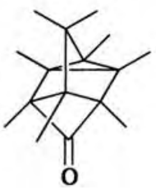
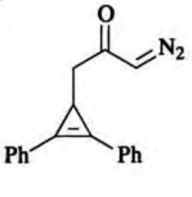
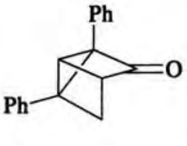
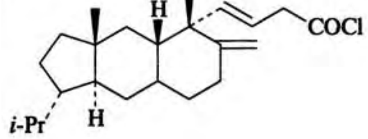
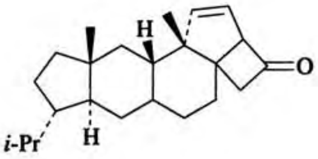
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	*i*-Pr_2NEt, 110°	 (57)	654
C_{16}			
	*hν*, MeOH	 (100)	655
C_{18}			
	*hν*, THF	 (—)	656
C_{23}			
	Et_3N, C_6H_6, reflux	 (80)	657

TABLE XIII. INTRAMOLECULAR CYCLOADDITIONS (*Continued*)

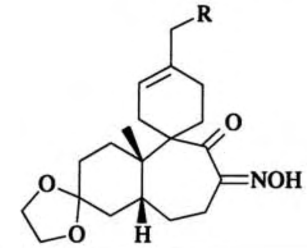
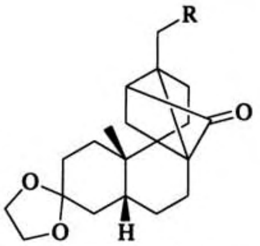
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	1. NH_2Cl, THF 2. *hν*, Et_2O, -75°		R = H (80) R = TMS (60)	658, 659, 652

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES

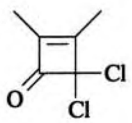
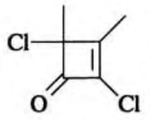
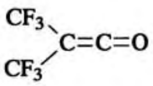
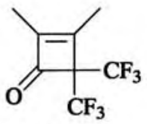
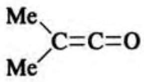
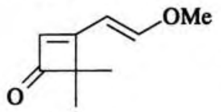
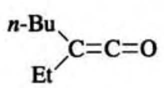
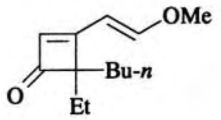
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
$MeC\equiv CMe$	Cl_3CCOCl	Zn-Cu, Et_2O 7 min	 (60) +  (2.5) **I** **II**	116
		Zn-Cu, $POCl_3$, Et_2O, 14 h	**I** (85)	111, 116
	$Cl_2CHCOCl$	Et_3N, 12-15°	**I** (12)	660
	 $(CF_3)_2C=C=O$	150°		661
	"	100°, 6 h	" (65)	661
C_5				
$HC\equiv CCH=CHOMe$	 $Me_2C=C=O$	MeCN	 (38)	115
	"	Et_2O, rt	" (65)	662
	 $(n\text{-}Bu)(Et)C=C=O$	MeCN, 82°	 (39)	662

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

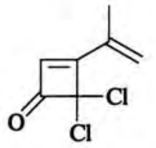
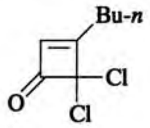
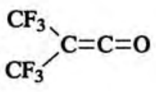
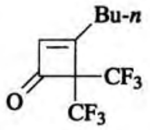
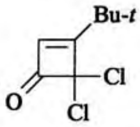
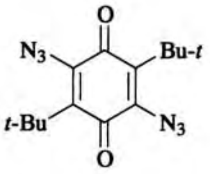
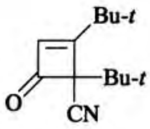
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$HC\equiv CC(Me)=CH_2$	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O, 14 h	 (45)	111, 113
C_6				
$HC\equiv CBu$-*n*	"	"	 (65-77)	111- 113
	"	Zn-Cu, Et_2O, 8 min	" (51)	116
		150°, 8 h	 (11.5)	661
$HC\equiv CBu$-*t*	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O, 10°, 14 h	 (80)	112
		C_6H_6	 (40-80)	663

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

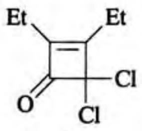
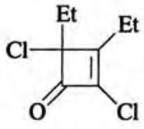
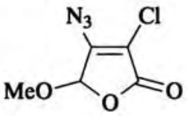
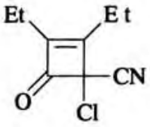
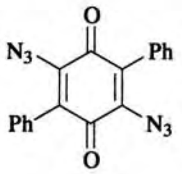
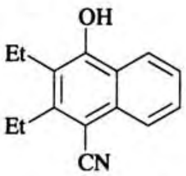
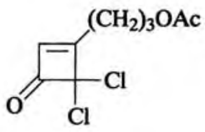
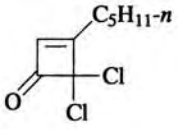
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$EtC\equiv CEt$	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O, 14 h	 (30) +  (56) I II	116
	"	"	I (57-62)	111, 113
		PhMe, 103°	 (61)	114
		CCl_4, 77°	 (33)	117
C_7				
$HC\equiv C(CH_2)_3OAc$	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O	 (80)	112
$HC\equiv CC_5H_{11}$-*n*	"	"	 (70)	113

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

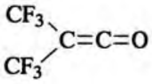
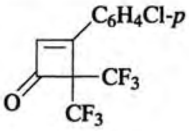
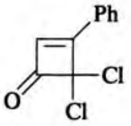
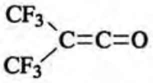
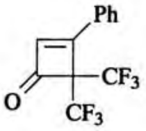
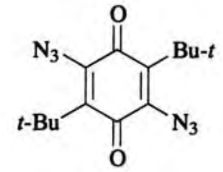
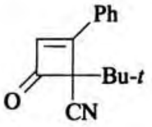
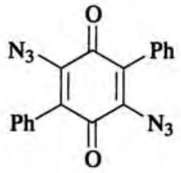
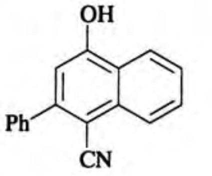
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
$HC{\equiv}CC_6H_4Cl\text{-}p$	 $(CF_3)_2C{=}C{=}O$	90°, 16 h	 (62)	661
	"	150°	" (—)	661
$HC{\equiv}CPh$	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O	 (75)	112, 113
	 $(CF_3)_2C{=}C{=}O$	100-150°	 (79-80)	148, 231, 387, 661
		C_6H_6	 (40-80)	663
		CCl_4, 77°	 (67)	117

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

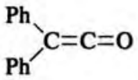
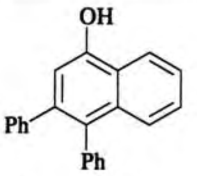
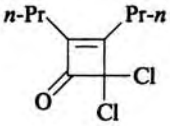
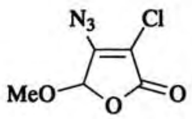
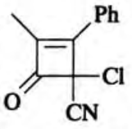
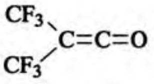
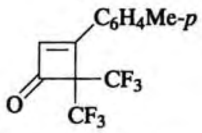
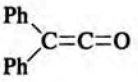
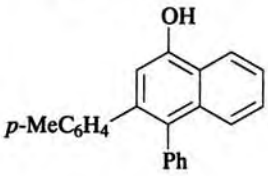
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	rt	 (81)	118
$n\text{-}PrC{\equiv}CPr\text{-}n$	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O, 10°, 4-26 h	 (—)	112
C_9				
$MeC{\equiv}CPh$		PhMe, 103°	 (84)	114
$HC{\equiv}CC_6H_4Me\text{-}p$	 $(CF_3)_2C{=}C{=}O$	150°	 (—)	661
	 $Ph_2C{=}C{=}O$	rt, 36 h	 (77)	664

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

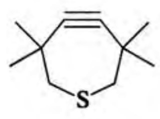
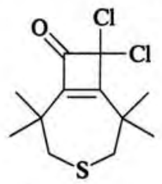
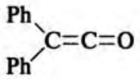
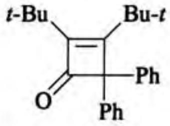
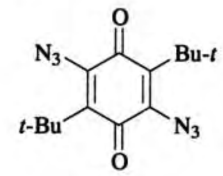
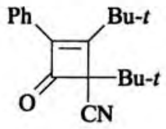
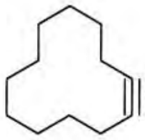
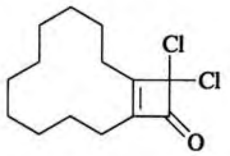
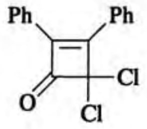
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}	 (80)	60
t-BuC≡CBu-t	 $Ph_2C{=}C{=}O$	175°, 5.5 h	 (47)	665
C_{12}				
t-BuC≡CPh		C_6H_6	 (40-80)	663
	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O, 10°, 4-26 h	 (—)	112
C_{14}				
PhC≡CPh	Cl_3CCOCl	Zn-Cu, $POCl_3$, Et_2O	 (32-45)	111, 113

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

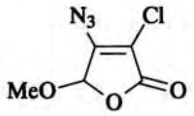
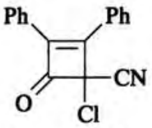
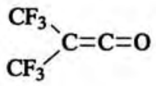
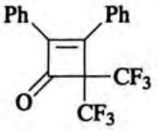
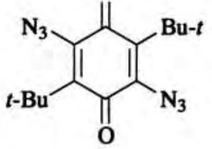
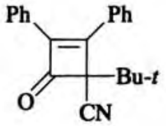
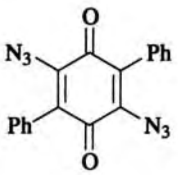
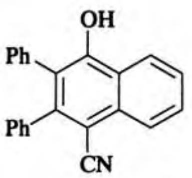
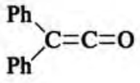
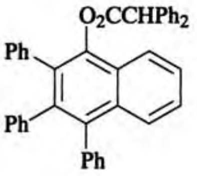
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 103°	 (77)	114
	 $(CF_3)_2C{=}C{=}O$	150-200°	 (95)	661
		C_6H_6	 (40-80)	663
		CCl_4, 77°	 (41)	117
	 $Ph_2C{=}C{=}O$	70-80°, 3 d	 (82)	119

TABLE XIV. [2+2] CYCLOADDITION OF KETENES TO ALKYNES (*Continued*)

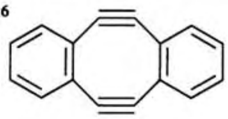
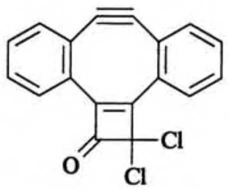
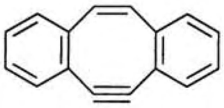
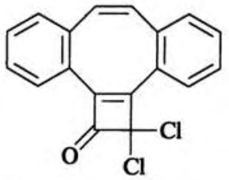
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{16} 	$Cl_2CHCOCl$	Et_3N, C_5H_{12}, 20°, 12 h	 (42)	666
	$Cl_2CHCOCl$	Et_3N, C_5H_{12}, 20°, 12 h	 (17)	666

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS

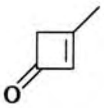
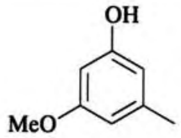
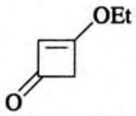
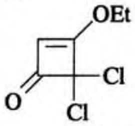
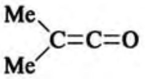
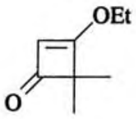
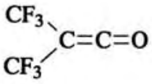
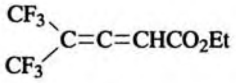
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
HC≡COMe		C_6H_6, 80-160° 26 h	 (71)	131
C_4				
HC≡COEt	$CH_2=C=O$	CH_2Cl_2, 0°	 (30-31)	126, 127
	$Cl_2CHCOCl$	Et_3N	 (—)	667
	 $Me_2C=C=O$	MeCN	 (57-80)	123-125, 668
	i-C_3H_7COCl	Et_3N, Et_2O, 0°	" (65-66)	126, 127
	$Me_2CBrCOBr$	Zn, EtOAc, 0°	" (58)	128
	 $(CF_3)_2C=C=O$	-80°	 $(CF_3)_2C=C=CHCO_2Et$ (39)	133

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

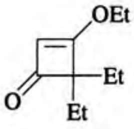
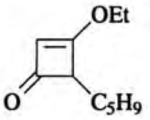
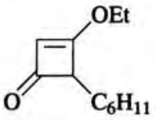
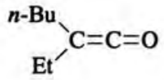
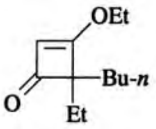
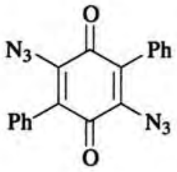
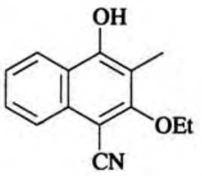
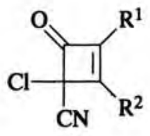
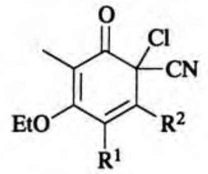
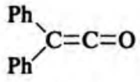
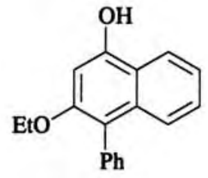
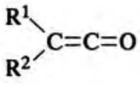
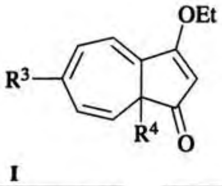
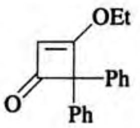
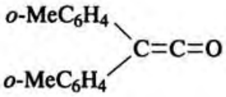
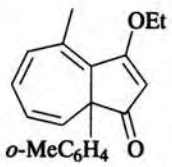
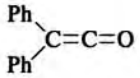
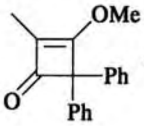
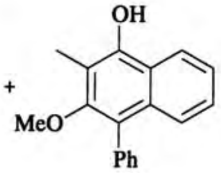
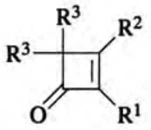
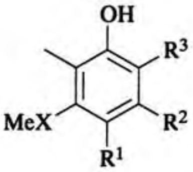
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Et_2CHCOCl$	Et_3N, 0°	 (10-30)	126
	$C_5H_9CH_2COCl$	Et_3N, 0°	 (10-30)	126
	$C_6H_{11}CH_2COCl$	Et_3N, 0°	 (10-30)	126
		C_6H_{14}, 25-40°	 (70)	123,124
		CCl_4, 77°	 (30)	117

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 40°	 R^1 R^2 Me Ph (33) Ph Ph (69) Et Et (85)	114
		C_6H_6, rt	 (35)	132
		$MeNO_2$, -18 to 20°	 I + II	

		I			II			I:II	
R^1	R^2	R^3	R^4	Yield	R^3	R^4	Yield		
Ph	Ph	H	Ph	(35)	—	—	(—)	—	132, 135-138
Ph	p-ClC_6H_4	H	p-ClC_6H_4	(—)	Cl	Ph	(—)	2.3	134
Ph	p-BrC_6H_4	H	p-BrC_6H_4	(—)	Br	Ph	(—)	2.4	134
Ph	p-$MeOC_6H_4$	H	p-$MeOC_6H_4$	(—)	MeO	Ph	(—)	50	134
Ph	p-MeC_6H_4	H	p-MeC_6H_4	(—)	Me	Ph	(—)	0.2	134
Ph	p-$EtO_2CC_6H_4$	H	p-$EtO_2CC_6H_4$	(—)	EtO_2C	Ph	(—)	22.2	134

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$(Ph)_2CHCOCl$	Et_3N, 0°	 (—)	126
	 $(o\text{-}MeC_6H_4)_2C{=}C{=}O$	$MeNO_2$, 0°	 (—)	134
$MeC{\equiv}COMe$	 $Ph_2C{=}C{=}O$	C_6H_6, 60°	 (24) +  (8)	132
$MeC{\equiv}CXMe$		C_6H_6 or PhMe, 80-160°, 2.5-21 h		131

X	R^1	R^2	R^3	
O	H	Me	Cl	(65)
O	H	Me	H	(92)
O	Me	Me	H	(61)
S	Me	Me	H	(86)
S	H	*n*-Bu	H	(82)

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

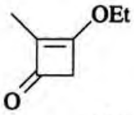
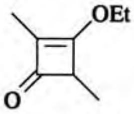
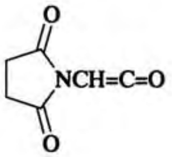
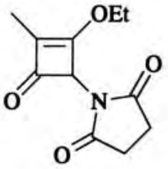
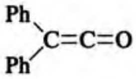
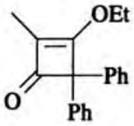
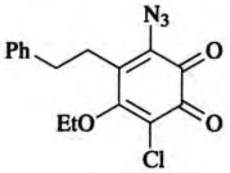
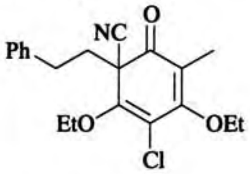
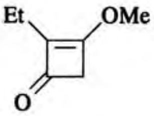
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
$MeC{\equiv}COEt$	$CH_2{=}C{=}O$	$MeNO_2$, 0°, 10 d	 (15)	669
	$MeC{\equiv}COEt$	140-150°	 (71)	129
		—	 (70)	670
	 $Ph_2C{=}C{=}O$	C_6H_6, rt	 (80)	129, 132
		C_6H_6, 66°	 (49)	671
$EtC{\equiv}COMe$	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (30)	672

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

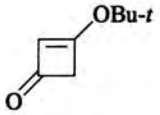
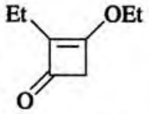
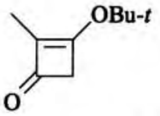
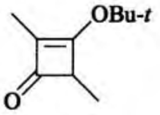
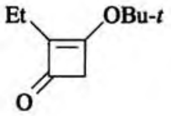
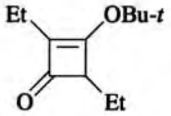
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
HC≡COBu-*t*	HC≡COBu-*t*	30°, 16 h	 (95)	673
EtC≡COEt	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (35)	672
C_7				
MeC≡COBu-*t*	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (51)	672
	MeC≡COBu-*t*	80-90°	 (—)	674
C_8				
EtC≡COBu-*t*	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (52)	672
	EtC≡COBu-*t*	80-90°	 (—)	674

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

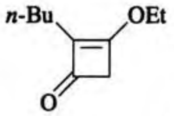
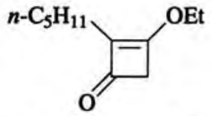
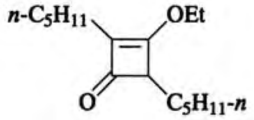
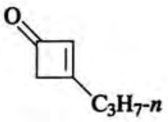
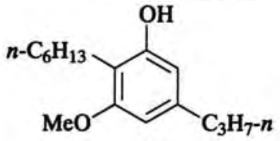
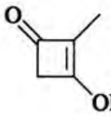
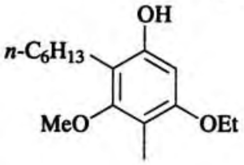
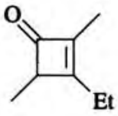
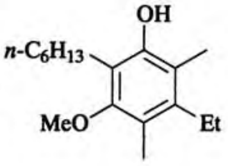
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
n-BuC≡COEt	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (34)	672
C_9				
n-C_5H_{11}C≡COEt	$CH_2{=}C{=}O$	$MeNO_2$, 0°	 (56)	672
	n-C_5H_{11}C≡COEt	120-130°	 (83)	129
n-C_6H_{13}C≡COMe		C_6H_6, 80-160°, 22 h	 (82)	675, 131
		C_6H_6, 80-160°, 22 h	 (71)	675, 131
		C_6H_6, 80-160°, 22 h	 (33)	675, 131

TABLE XV. [2+2] CYCLOADDITION OF KETENES TO ACETYLENIC ETHERS (*Continued*)

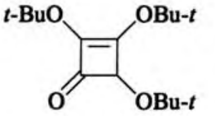
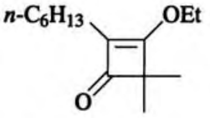
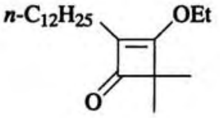
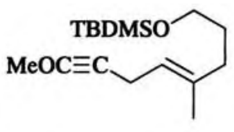
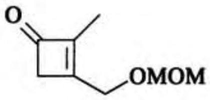
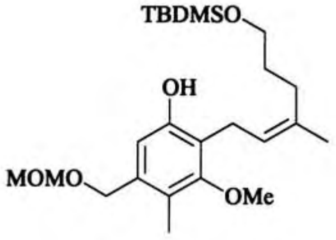
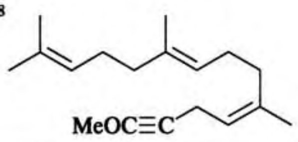
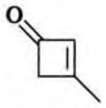
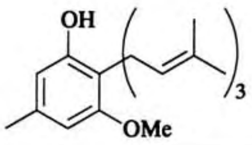
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
t-BuOC≡COBu-t	t-BuOC≡COBu-t	C_6H_6, 80°	 (100)	130
n-$C_6H_{13}C\equiv COEt$	$Me_2CBrCOBr$	Zn, EtOAc, 0°	 (68)	128
C_{16}				
n-$C_{12}H_{25}C\equiv COEt$	$Me_2CBrCOBr$	Zn, EtOAc, 0°	 (—)	128
		C_6H_6, 120°, 14 h	 (73)	676
C_{18}				
		C_6H_6, 80°, 4 h	 (65)	131

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES

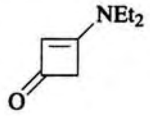
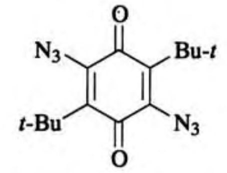
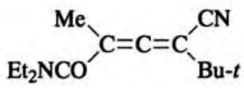
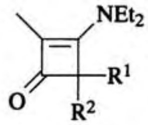
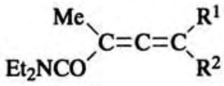
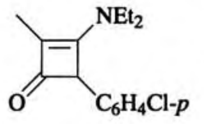
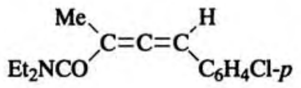
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
$MeC{\equiv}CNEt_2$	$CH_2{=}C{=}O$	Et_2O, -50°	 (7)	139
		C_6H_6, 80°	 (53)	142
	$R^1R^2CHCOCl$	Et_3N	 I +  II	
	R^1 R^2		I II	
	Me CO_2Et		(3) (66)	278
	Me CO_2NEt_2		(3) (95)	278
	Ph CO_2Et		(32) (32)	278
	Ph H		(37) (9)	140, 677
	$p\text{-}ClC_6H_4COCHN_2$	hν, C_6H_6	 (15) +  (25)	140

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES (*Continued*)

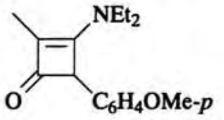
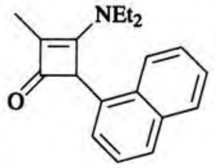
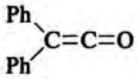
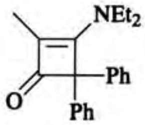
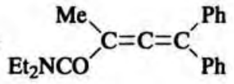
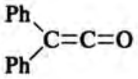
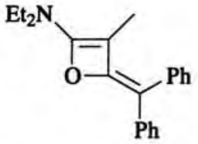
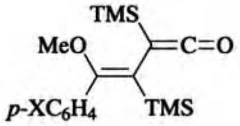
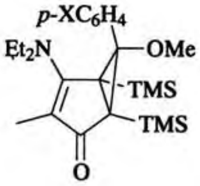
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	p-MeOC$_6$H$_4$COCHN$_2$	$h\nu$, C$_6$H$_6$	 (42)	140
		Et$_3$N, Et$_2$O, rt	 (—)	677
	 $Ph_2C{=}C{=}O$	C$_6$H$_6$, 15°	 +  $Me(Et_2NCO)C{=}C{=}CPh_2$ I (16) II (57)	140
	 $Ph_2C{=}C{=}O$	C$_6$H$_6$	I (11) +  (27)	678
		C$_6$H$_{14}$, 25°, 3 h	 X: H (—); Me (—); CF$_3$ (38)	143 143 143, 144

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES (*Continued*)

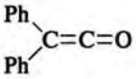
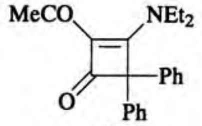
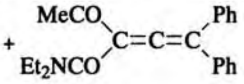
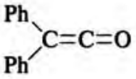
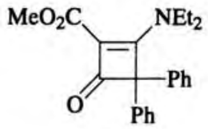
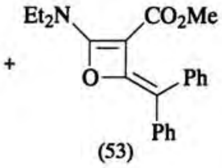
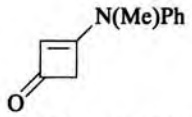
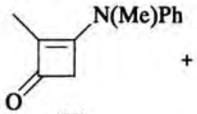
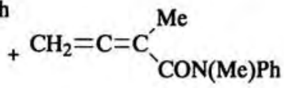
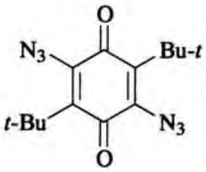
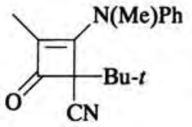
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$				
MeCOC≡CNEt$_2$	 $Ph_2C{=}C{=}O$	C$_6$H$_6$, 15°	 +  $MeCO(Et_2NCO)C{=}C{=}CPh_2$ (7) (11)	140
MeO$_2$CC≡CNEt$_2$	 $Ph_2C{=}C{=}O$	C$_6$H$_6$	 +  (15) (53)	678
C$_9$				
HC≡CN(Me)Ph	CH$_2$=C=O	MeCN	 (7) + CH$_2$=C=CHCON(Me)Ph (34)	679
C$_{10}$				
MeC≡CN(Me)Ph	CH$_2$=C=O	MeCN	 +  $CH_2{=}C{=}C(Me)CON(Me)Ph$ (50) (12)	679
		C$_6$H$_6$, 80°	 (23)	142

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES (*Continued*)

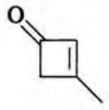
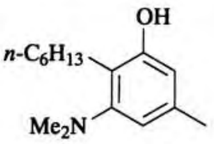
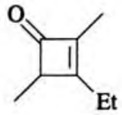
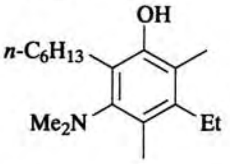
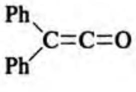
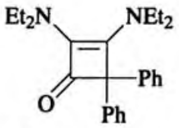
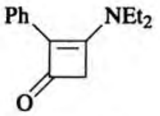
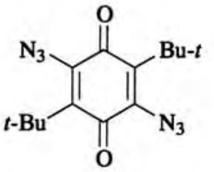
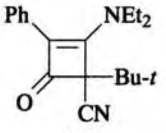
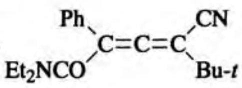
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$n\text{-}C_6H_{13}C{\equiv}CNMe_2$		C_6H_6, 150°, 2 h	 (74)	131
		C_6H_6, 160°, 3 h	 (83)	131
$Et_2NC{\equiv}CNEt_2$	 $Ph_2C{=}C{=}O$	Et_2O, -50°	 (94)	139
C_{12}				
$PhC{\equiv}CNEt_2$	$CH_2{=}C{=}O$	Et_2O, -50°	 (78)	139
		C_6H_6, 80°	 +  $Et_2NCO(Ph)C{=}C{=}C(CN)Bu\text{-}t$ (45) (5)	142

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES (*Continued*)

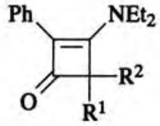
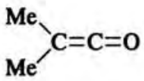
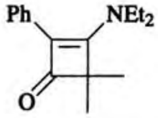
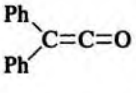
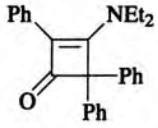
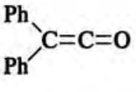
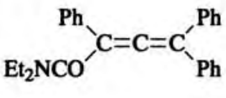
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$R^1R^2CHCOCl$	Et_3N, Et_2O, rt		
	R^1 R^2			
	H H		(—)	677
	H Me		(—)	677
	Me CO_2Et		(14)	278
	Me $CONEt_2$		(21)	278
	H Ph		(—)	677
	Ph CO_2Et		(65)	278
	Ph Et		(57)	677
	H $C_{10}H_7\text{-}1$		(—)	677
	 $Me_2C{=}C{=}O$	THF, 0°	 (17)	678
	 $Ph_2C{=}C{=}O$	Et_2O, -50°	 I (95)	139
	 $Ph_2C{=}C{=}O$	C_6H_6, 15°	I (54) +  $Et_2NCO(Ph)C{=}C{=}CPh_2$ (14)	140

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES *(Continued)*

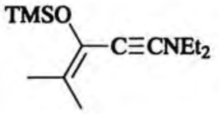
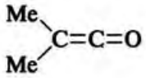
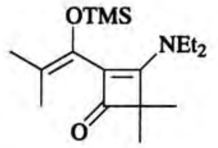
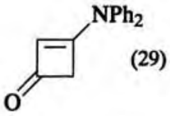
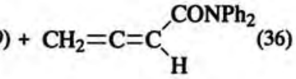
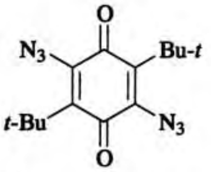
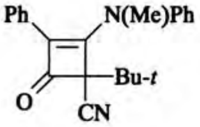
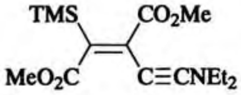
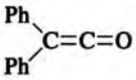
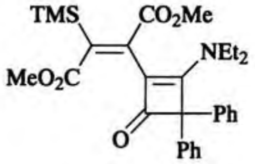
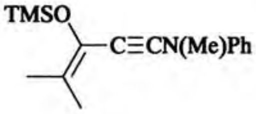
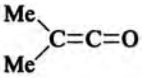
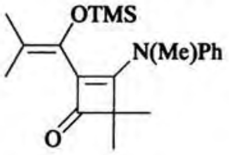
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13}				
		Et_2O	 (10)	141
C_{14}				
$HC\equiv CNPh_2$	$CH_2=C=O$	MeCN	 (29) +  $CH_2=C=CH(CONPh_2)$ (36)	679
C_{15}				
$PhC\equiv CN(Me)Ph$		C_6H_6, 80°	 (15)	142
		Et_2O	 (—)	680
C_{16}				
		Et_2O	 (38)	141

TABLE XVI. [2+2] CYCLOADDITION OF KETENES TO YNAMINES *(Continued)*

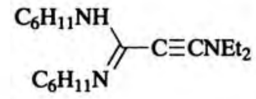
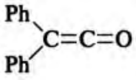
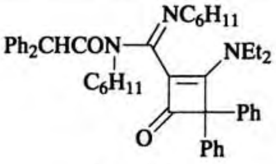
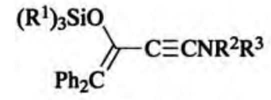
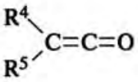
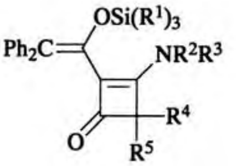
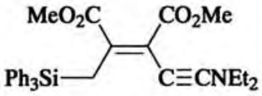
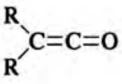
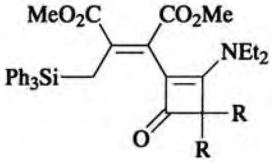
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{19}				
		Et_2O	 (36)	681
C_{23-41}				
		Et_2O		141
R^1 R^2 R^3	R^4 R^5			
Me Et Et	Me Me		(60)	
Me Et Et	Me Ph		(37)	
Me Et Et	Ph Ph		(61)	
Me Me Ph	Ph Ph		(68)	
Ph Me Ph	Ph Ph		(43)	
		—		682
	R			
	H		(—)	
	Me		(—)	
	Ph		(—)	

TABLE XVII. CYCLOADDITION OF KETENES TO ORGANOMETALLIC ACETYLENES

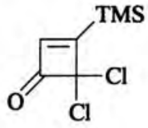
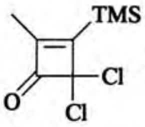
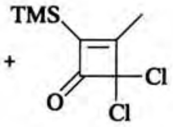
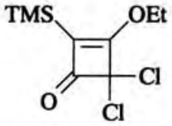
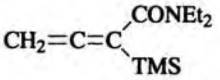
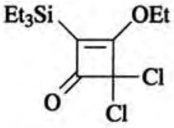
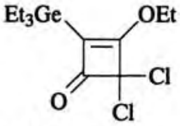
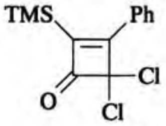
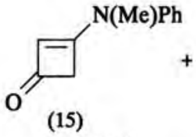
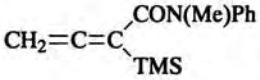
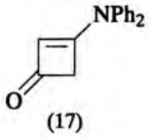
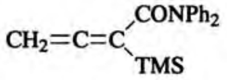
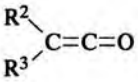
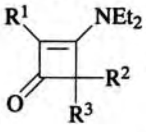
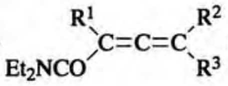
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
HC≡CTMS	Cl_3CCOCl	Zn, Et_2O	 (66)	120
	"	Zn, $POCl_3$, Et_2O	" (60)	113
C_6				
MeC≡CTMS	"	Zn, Et_2O	 I (27) +  II (47)	120
	"	Zn, $POCl_3$, Et_2O	I (30) + II (30)	113
C_7				
EtOC≡CTMS	"	Zn, $POCl_3$, Et_2O	 (86)	120
	$Cl_2CHCOCl$	Et_3N, Et_2O	" (—)	121
C_9				
TMSC≡CNEt$_2$	$CH_2=C=O$	MeCN	 $CH_2=C=C\genfrac{}{}{0pt}{}{CONEt_2}{TMS}$ (17)	683
C_{10}				
$Et_3SiC≡COEt$	$Cl_2CHCOCl$	Et_3N, Et_2O	 (—)	121

TABLE XVII. CYCLOADDITION OF KETENES TO ORGANOMETALLIC ACETYLENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$Et_3GeC≡COEt$	$Cl_2CHCOCl$	Et_3N, Et_2O	 (—)	121
C_{11}				
PhC≡CTMS	Cl_3CCOCl	Zn, Et_2O	 (93)	120
C_{12}				
TMSC≡CN(Me)Ph	$CH_2=C=O$	MeCN	 (15) +  $CH_2=C=C\genfrac{}{}{0pt}{}{CON(Me)Ph}{TMS}$ (23)	683
C_{17}				
TMSC≡CNPh$_2$	$CH_2=C=O$	MeCN	 (17) +  $CH_2=C=C\genfrac{}{}{0pt}{}{CONPh_2}{TMS}$ (39)	683
C_{18}				
$R^1C≡CNEt_2$	 $\genfrac{}{}{0pt}{}{R^2}{R^3}C=C=O$	—	 I +  $\genfrac{}{}{0pt}{}{R^1}{Et_2NCO}C=C=C\genfrac{}{}{0pt}{}{R^2}{R^3}$ II	140

R^1	R^2	R^3	I	II
Ph_2P	Ph	Ph	(10)	(0)
$Ph_2P(O)$	H	Ph	(35)	(12)
$Ph_2P(O)$	Ph	Ph	(12)	(0)
$Ph_2P(S)$	Ph	Ph	(49)	(0)
$Ph_2P(NTs)$	Ph	Ph	(6)	(0)

TABLE XVII. CYCLOADDITION OF KETENES TO ORGANOMETALLIC ACETYLENES (*Continued*)

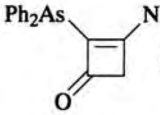
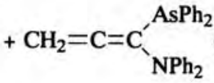
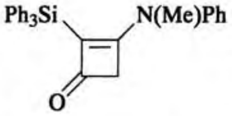
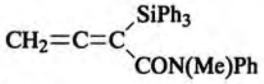
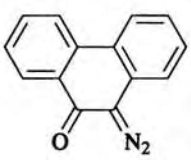
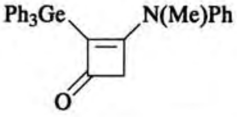
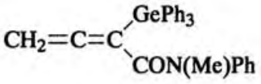
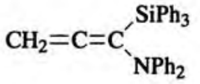
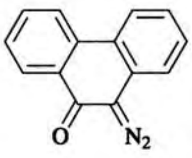
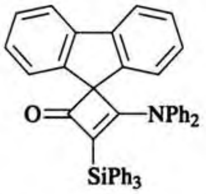
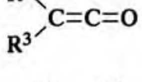
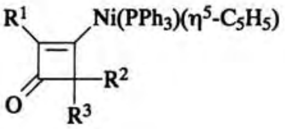
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{26}				
$Ph_2AsC{\equiv}CNPh_2$	$CH_2{=}C{=}O$	MeCN	 (4.5) +  $CH_2{=}C{=}C(AsPh_2)(NPh_2)$ (33)	679
C_{27}				
$Ph_3SiC{\equiv}CN(Me)Ph$	$CH_2{=}C{=}O$	MeCN	 (6) +  $CH_2{=}C{=}C(SiPh_3)CON(Me)Ph$ (7)	683
		$h\nu$, C_6H_6	 (19)	141
$Ph_3GeC{\equiv}CN(Me)Ph$	$CH_2{=}C{=}O$	MeCN	 (8) +  $CH_2{=}C{=}C(GePh_3)CON(Me)Ph$ (35)	679
C_{32}				
$Ph_3SiC{\equiv}CNPh_2$	$CH_2{=}C{=}O$	MeCN	 $CH_2{=}C{=}C(SiPh_3)(NPh_2)$ (41)	683

TABLE XVII. CYCLOADDITION OF KETENES TO ORGANOMETALLIC ACETYLENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		$h\nu$, C_6H_6	 (12)	141
$R^1C{\equiv}CNi(PPh_3)(\eta^5\text{-}C_5H_5)$	 $R^2R^3C{=}C{=}O$	C_6H_6		122

R^1	R^2	R^3	
H	H	H	(27)
H	Me	Ph	(72)
H	Ph	Ph	(32)
Me	Ph	Ph	(82)
$CH{=}CH_2$	Ph	Ph	(70)
Ph	H	H	(84)
Ph	Me	H	(68)
Ph	Ph	H	(73)
Ph	Ph	Ph	(78)
C_6H_4Br-*p*	Ph	Ph	(62)
C_6H_4Me-*p*	Ph	Ph	(80)

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES

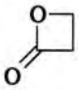
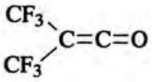
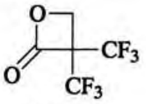
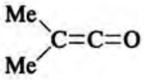
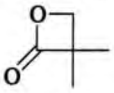
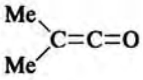
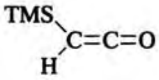
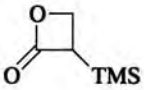
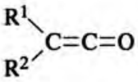
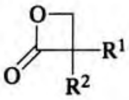
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
HCHO	$CH_2=C=O$	$AlCl_3$, $ZnCl_2$, EtOAc, 10°	 (—)	684
	$CH_2=C=O$	$AlCl_3$, Me_2CO, β-propiolactone	" (93)	685, 686
	 $(CF_3)_2C=C=O$	$ZnCl_2$, Et_2O, 150°	 (—)	148
	 $Me_2C=C=O$	$AlCl_3$, I_2, glyme, 50°	 (89)	687
	 $Me_2C=C=O$	$HgCl_2$, i-PrOAc, 50-55°	" (93)	149
	 $TMS(H)C=C=O$	BF_3•Et_2O, 20°	 (30)	147
	 $R^1R^2C=C=O$	$ZnCl_2$, i-PrOAc, 50°		
	R^1 R^2			
	Me Et		(72)	149
	Et Et		(—)	149
	Me n-Pr		(—)	149
	Et n-Bu		(49)	149
	t-Bu t-Bu		(68)	688

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

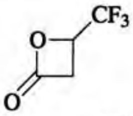
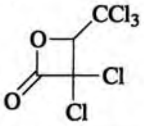
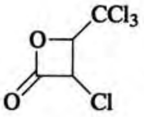
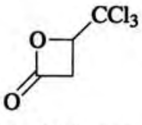
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
CF_3CHO	MeCOCl	Et_3N, Et_2O, 0-10°	 (20)	168
Cl_3CCHO	$Cl_2CHCOCl$	Et_3N, Et_2O or C_6H_{14}, 0-25°	 (39-43)	168
	$Cl_2CHCOCl$	(–)-Brucine, CCl_4, -20°	" (–)-isomer (72)	169
	$ClCH_2COCl$	Et_3N, Et_2O or C_6H_{14}	 (40) *cis*:*trans* = 1.60-1.64	150, 166
	MeCOCl	Et_3N, Et_2O	 (69)	168
	MeCOCl	(–)-PhCH(NMe_2)Me, Et_2O, 0°	" (–)-isomer (72)	169
	$CH_2=C=O$	rt	" (70-92)	175, 689
	$CH_2=C=O$	BF_3•Et_2O, CH_2Cl_2, -60°	" (70-92)	690
	$CH_2=C=O$	(–)-Brucine, $CHCl_3$, -25°	" (+)-isomer (—)	169
	$CH_2=C=O$	Quinidine, PhMe, -50°	" (89-95) *R*, 98% ee	170, 171, 174

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

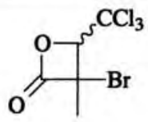
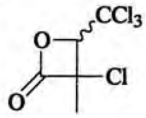
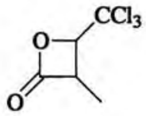
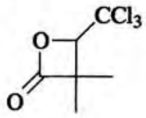
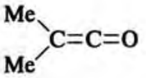
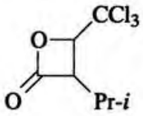
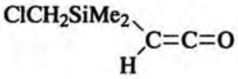
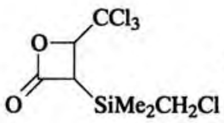
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeCHBrCOCl	Et_3N, C_6H_{14}, rt	 (60)	151
	MeCHClCOCl	Et_3N, C_6H_{14}, rt	 (53)	151
	EtCOCl	Et_3N, C_6H_{14}, rt	 (43) *cis:trans* = 1.39	150
	i-PrCOCl	Et_3N, Et_2O	 (15-65)	166, 689
	 $Me_2C{=}C{=}O$	$BF_3{\cdot}Et_2O$, -15°	" (60)	689
	i-PrCHBrCOCl	Zn, Et_2O	 (25) *cis:trans* = 0.9	166
	 $ClCH_2SiMe_2(H)C{=}C{=}O$	$BF_3{\cdot}Et_2O$, -50°	 (51) *cis:trans* = 0.25	147

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

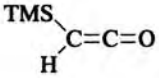
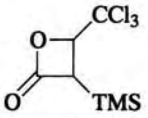
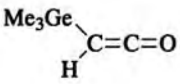
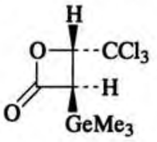
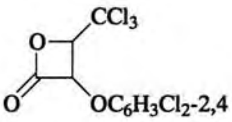
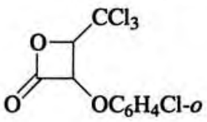
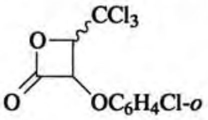
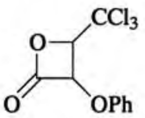
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $TMS(H)C{=}C{=}O$	$BF_3{\cdot}Et_2O$, 90°	 (69) *cis:trans* = 0.25	147
	 $Me_3Ge(H)C{=}C{=}O$	$BF_3{\cdot}Et_2O$, 50°	 (67)	147
	2,4-$Cl_2C_6H_3OCH_2COCl$	Et_3N, Et_2O, 0-10°	 (63)	147
	o-$ClC_6H_4OCH_2COCl$	(–)-Brucine, $CHCl_3$, -25°	 (45) (–)-isomer	168, 169
	o-$ClC_6H_4OCH_2COCl$	Et_3N, Et_2O, 0-10°	 (45)	168
	$C_6H_5OCH_2COCl$	Et_3N, Et_2O, 0-10°	 (36)	168
	$C_6H_5OCH_2COCl$	Et_3N, Et_2O, 0-10°	" (61) *cis:trans* = 1.7	691

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

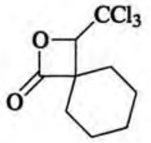
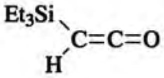
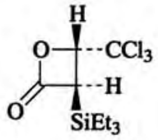
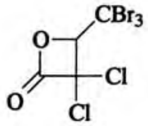
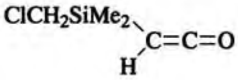
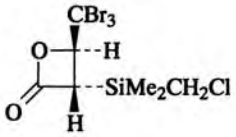
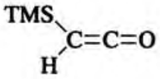
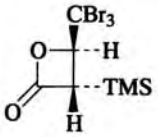
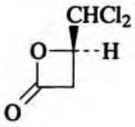
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$C_6H_{11}COCl$	Et_3N, C_6H_6	 (—)	527
	 $Et_3Si(H)C{=}C{=}O$	BF_3•Et_2O, 90°	 (45)	147
Br_3CCHO	$Cl_2CHCOCl$	Et_3N, Et_2O, 0-10°	 (11)	168
	 $ClCH_2SiMe_2(H)C{=}C{=}O$	BF_3•Et_2O, -10°	 (64)	147
	 $TMS(H)C{=}C{=}O$	BF_3•Et_2O, -10°	 (63)	147
Cl_2CHCHO	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (67)	171

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

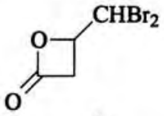
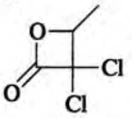
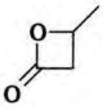
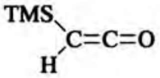
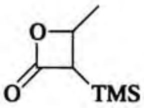
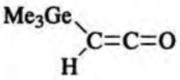
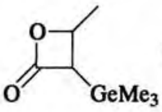
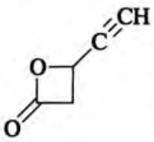
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
Br_2CHCHO	$CH_2{=}C{=}O$	BF_3•Et_2O, CH_2Cl_2, -70°	 (54)	690
MeCHO	$Cl_2CHCOCl$	Et_3N, Et_2O, 10°	 (51)	324, 692
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 0°	" (—)	693
	$CH_2{=}C{=}O$	BF_3•Et_2O, Et_2O, -20°	 (80)	158
	$CH_2{=}C{=}O$	SiO_2/Al_2O_3, 10-15°	" (90)	694, 695
	 $TMS(H)C{=}C{=}O$	BF_3•Et_2O, 20°	 (64) *cis*:*trans* = 1.5	147
	 $Me_3Ge(H)C{=}C{=}O$	BF_3•Et_2O, -78°	 (75)	147
C_3				
$HC{\equiv}CCHO$	$CH_2{=}C{=}O$	BF_3•Et_2O, Et_2O, -20°	 (40)	158

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

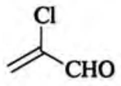
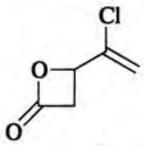
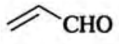
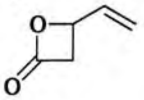
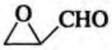
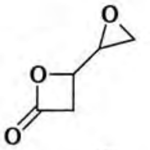
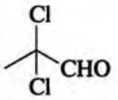
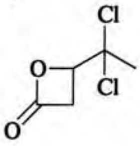
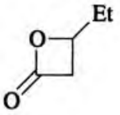
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	$BF_3•Et_2O$, Et_2O, -20°	 (45)	158
	$CH_2=C=O$	$BF_3•Et_2O$, Et_2O, -20°	 (87)	696
	$CH_2=C=O$	$BF_3•Et_2O$, PhMe, -25°	" (72)	697
	$CH_2=C=O$	$ZnCl_2$, Et_2O, 0-10°	 (42)	159, 160
	MeCOCl	Et_3N, Et_2O, 0°	 (5)	175
	$CH_2=C=O$	Quinidine, PhMe, -25°	" (95) *R*, 91% ee	171, 175
	$CH_2=C=O$	Brucine, PhMe, -25°	" (15)	175
EtCHO	$CH_2=C=O$	$BF_3•Et_2O$, Et_2O, -20°	 (75)	158

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

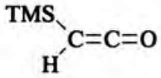
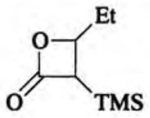
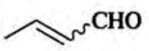
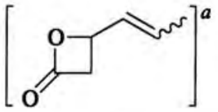
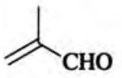
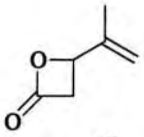
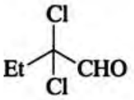
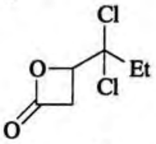
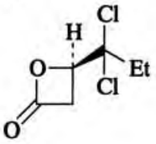
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $TMS(H)C=C=O$	$BF_3•Et_2O$	 (60)	698
	"	$BF_3•Et_2O$	" (68) *cis:trans* = 1.5	147
C_4				
	$CH_2=C=O$	ZnO_2CPr, PhMe	 (—)	164
	$CH_2=C=O$	$BF_3•Et_2O$, Et_2O, -20°	 (70)	158
	$CH_2=C=O$	$BF_3•Et_2O$, Et_2O, 10°	 (49)	176
	$CH_2=C=O$	Quinidine, PhMe, -25°	 (72-95) 89-100% ee	171, 173, 176

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

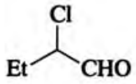
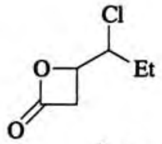
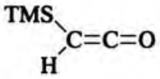
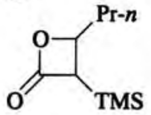
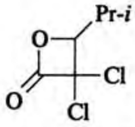
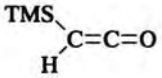
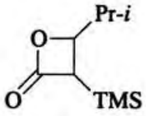
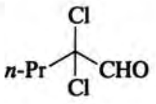
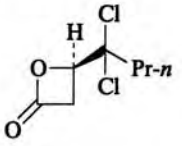
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	BF_3•Et_2O, CH_2Cl_2, -60°	 (60)	690
n-PrCHO		BF_3•Et_2O	 (54)	698
	"	BF_3•Et_2O, Et_2O, 20°	" (62) *cis:trans* = 1.5	147
i-PrCHO	$Cl_2CHCOCl$	Et_3N, Et_2O, 10-20°	 (40)	324, 692
		BF_3•Et_2O	 (56)	698
	"	"	" (90) *cis:trans* = 1.5	147
C_5				
	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (66) 84% ee	176

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

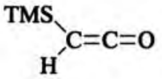
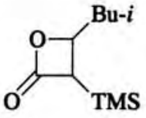
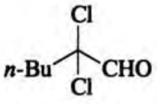
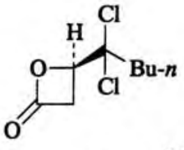
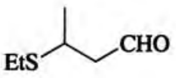
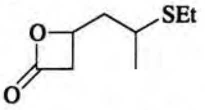
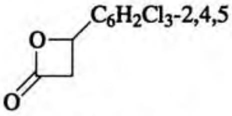
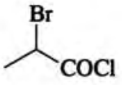
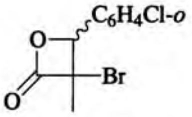
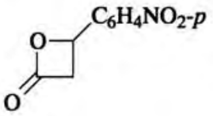
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
i-BuCHO		BF_3•Et_2O, Et_2O, 20°	 (86) *cis:trans* = 1.5	147
C_6				
	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (90-95) >98% ee	173
	$CH_2{=}C{=}O$	BF_3•Et_2O, Et_2O, 20°	 (72)	323
C_7				
2,4,5-$Cl_3C_6H_2CHO$	$CH_2{=}C{=}O$	BF_3•Et_2O, PhMe, 0°	 (65)	699
o-ClC_6H_4CHO		Et_3N, C_6H_{14}, rt	 (50)	151
p-$O_2NC_6H_4CHO$	$CH_2{=}C{=}O$	BF_3•Et_2O, PhMe, 0°	 (79)	699

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

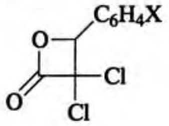
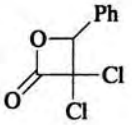
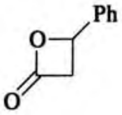
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
XC_6H_4CHO	$Cl_2CHCOCl$	Et_3N, $ZnCl_2$, Et_2O, 3-25°		
X				
H			(55)	161
o-Cl			(53)	161
m-Cl			(59)	161
p-Cl			(59-66)	161, 324, 692
o-NO_2			(85)	161
m-NO_2			(71)	161
p-NO_2			(65)	161
p-CN			(82)	161
o-Me			(37)	161
m-Me			(53)	161
p-Me			(44)	161
m-MeO			(38)	161
p-MeO			(23)	161
m-AcO			(44)	161
p-AcO			(29)	161
PhCHO	$Cl_2CHCOCl$	Et_3N, Et_2O, 10°	 (30)	324, 692
	$CH_2{=}C{=}O$	$BF_3{\cdot}Et_2O$, PhMe, 4 h	 (95-96)	700, 699

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

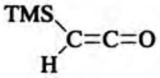
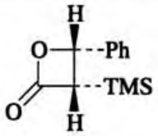
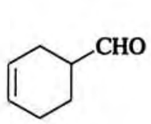
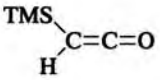
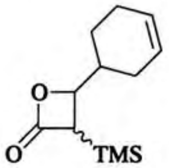
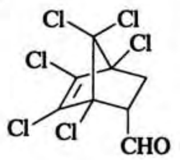
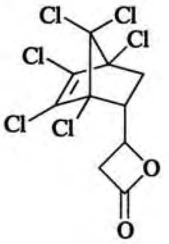
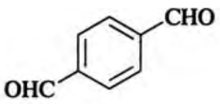
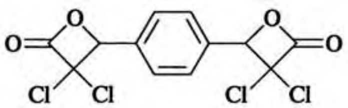
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(TMS)(H)C{=}C{=}O$	$BF_3{\cdot}Et_2O$, -50°	 (65)	167
	 $(TMS)(H)C{=}C{=}O$	$BF_3{\cdot}Et_2O$, -50°	 (65) *cis:trans* = 2	698
C_8				
	$CH_2{=}C{=}O$	$ZnCl_2$, EtOAc, -50°	 (21)	701
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (33)	702

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

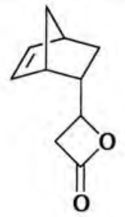
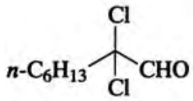
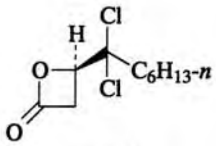
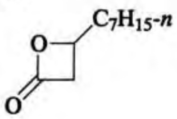
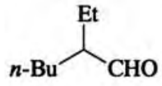
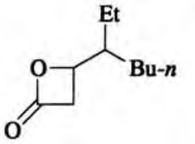
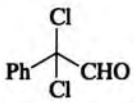
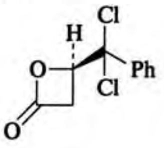
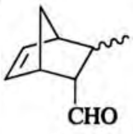
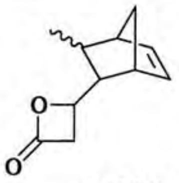
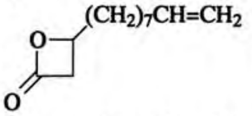
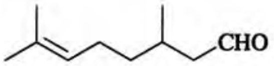
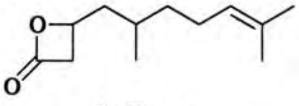
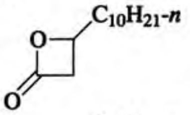
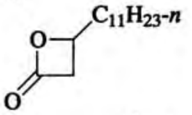
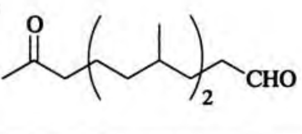
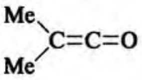
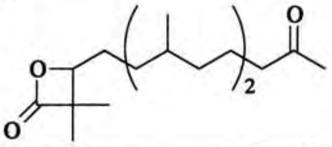
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	ZnCl, 80°	 (—)	703
 $n\text{-}C_6H_{13}CCl_2CHO$	$CH_2=C=O$	Quinidine, PhMe, -25°	 (90-95) >98% ee	173
$n\text{-}C_7H_{15}CHO$	$CH_2=C=O$	—	 (>84)	704
	$CH_2=C=O$	$BF_3•Et_2O$, THF, -60 to -70°	" (—)	705
	$CH_2=C=O$	$BF_3•Et_2O$, THF, -60 to -70°	 (50)	706, 705
 $PhCCl_2CHO$	$CH_2=C=O$	Quinidine, PhMe, -25°	 (89) 90% ee	171

TABLE XVIII. [2+2] CYCLOADDITION OF KETENES TO ALDEHYDES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	$CH_2=C=O$	$AlCl_3$, $ZnCl_2$, EtOAc, <20°	 (—)	703
C_{10}				
$CH_2=CH(CH_2)_7CHO$	$CH_2=C=O$	$BF_3•Et_2O$, THF, -70 to -60°	 (—)	705
	$CH_2=C=O$	BF_3, THF	 (49)	707
C_{11}				
$n\text{-}C_{10}H_{21}CHO$	$CH_2=C=O$	$BF_3•Et_2O$, THF, -70 to -60°	 (—)	705
C_{12}				
$n\text{-}C_{11}H_{23}CHO$	$CH_2=C=O$	$BF_3•Et_2O$, THF, -70 to -60°	 (95.6)	705
C_{15}				
	 $Me_2C=C=O$	—	 (>82)	162

---

[a] This product polymerizes.

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES

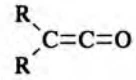
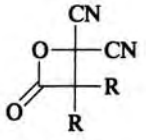
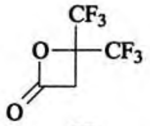
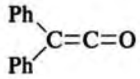
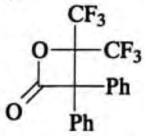
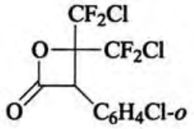
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
$CO(CN)_2$	 $R_2C{=}C{=}O$	—		
	R	Solvent		
	H	C_6H_6	(81.6)	145, 708
	Me	Et_2O	(86)	145
	Et	C_6H_{14}	(—)	145
	n-Pr	C_6H_{14}	(80)	145
$CO(CF_3)_2$	$CH_2{=}C{=}O$	Et_2O, -78°	 (96)	146
	 $Ph_2C{=}C{=}O$	KF, MeCN	 (59)	709
$CO(CF_2Cl)_2$	*o*-$ClC_6H_4CH_2COCl$	(–)-Brucine, $CHCl_3$, -30°	 (—) (+)-isomer	169

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

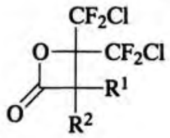
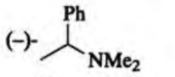
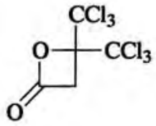
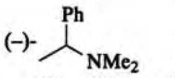
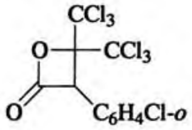
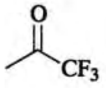
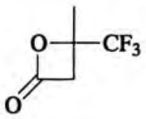
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$R^1R^2CHCOCl$			
	R^1 R^2			
	H Cl	Et_3N, C_6H_{14}, rt	(52)	151
	Me Cl	Et_3N, C_6H_{14}, rt	(55)	151
	Me Br	Et_3N, C_6H_{14}, rt	(60)	151
	H *o*-ClC_6H_4	(–)-Brucine, $CHCl_3$ -35°	(—), racemic	169
	H *o*-ClC_6H_4	 CCl_4, -30°	(—), (–)-isomer	169
$CO(CCl_3)_2$	MeCOCl	Et_3N, Et_2O, 0°	 (6)	168
	$CH_2{=}C{=}O$	190°	" (80-85)	689,710, 711
	o-$ClC_6H_4CH_2COCl$	 CCl_4, -20°	 (—)	169
	$CH_2{=}C{=}O$	BF_3 45Et_2O, (*i*-Pr)$_2$O, -70°	 (57)	690

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

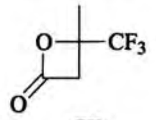
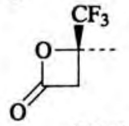
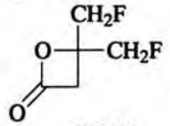
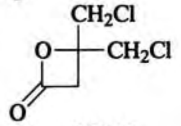
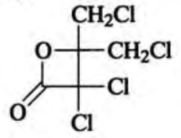
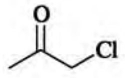
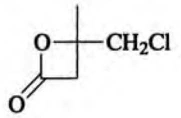
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	$BF_3{\bullet}Et_2O$, Et_2O, 0°	 (72)	712
	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (83)	171, 172
$CO(CH_2F)_2$	$CH_2{=}C{=}O$	$ZnCl_2$, Et_2O, 25-30°	 (95)	713
$CO(CH_2Cl)_2$	$CH_2{=}C{=}O$	$BF_3{\bullet}Et_2O$, CH_2Cl_2, -30°	 (85)	690
	Cl_3CCOCl	Zn, Et_2O, rt	 (23)	151
	$CH_2{=}C{=}O$	$BF_3{\bullet}Et_2O$, $CHCl_3$, -30°	 (80)	690
	$CH_2{=}C{=}O$	$BF_3{\bullet}Et_2O$, Et_2O, -15°	" (75)	714

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

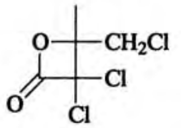
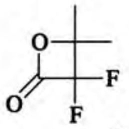
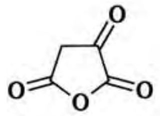
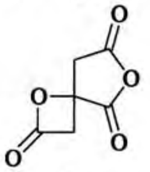
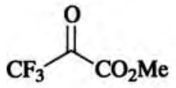
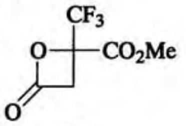
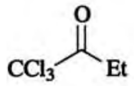
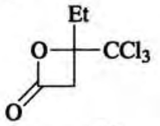
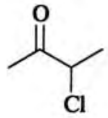
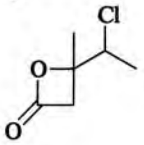
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O, rt	 (15)	151
$COMe_2$	$F_2BrCCOCl$	Zn, Me_2CO, -10°	 (50)	715
	$CH_2{=}C{=}O$	$ZnCl_2$, 0°	 (—)	716
	$CH_2{=}C{=}O$	Et_2O, -70°	 (36)	717
	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (1-2)	171
	$CH_2{=}C{=}O$	$BF_3{\bullet}Et_2O$, Et_2O, -15°	 (84)	714

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

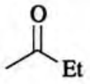
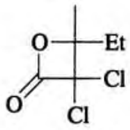
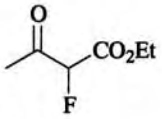
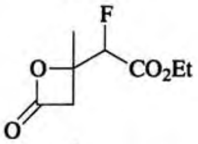
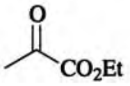
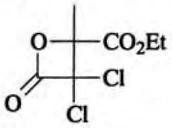
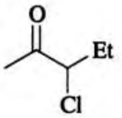
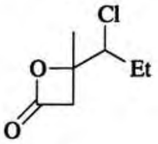
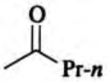
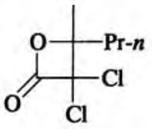
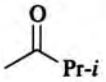
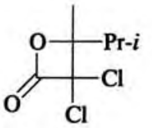
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O, rt	 (35)	151
	$CH_2=C=O$	$ZnCl_2$, $CHCl_3$, 5°	 (45)	713
	$Cl_2CHCOCl$	Et_3N, Et_2O, 10°	 (33)	692
	$CH_2=C=O$	BF_3•Et_2O, Et_2O, -15°	 (—)	714
C_5				
	Cl_3CCOCl	Zn, Et_2O, rt	 (35)	151
	Cl_3CCOCl	Zn, Et_2O, rt	 (20)	151

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

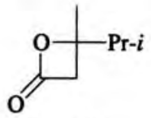
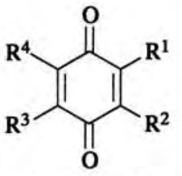
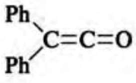
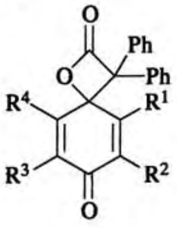
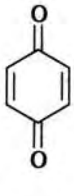
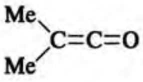
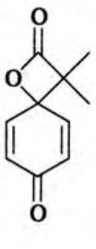
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	BF_3•Et_2O, CCl_4, 0°	 (—)	156
	 $Ph_2C=C=O$	Et_2O, pet. ether		
R^1 R^2 R^3 R^4				
Cl Cl Cl Cl			(38)	153
Cl Cl Cl H			(61)	152
H Cl Cl H			(70)	152
Cl H Cl H			(56)	152
H Br Br H			(78)	152
H Cl H H			(74)	152
H H H H			(57)	718
	 $Me_2C=C=O$	THF, 0°	 (64)	165

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

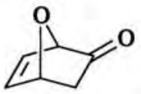
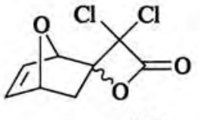
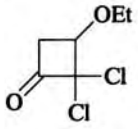
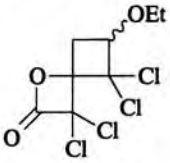
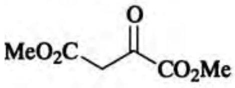
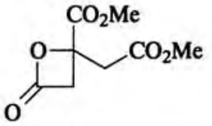
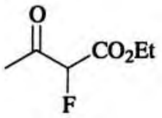
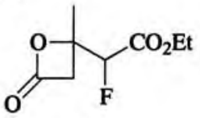
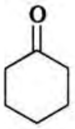
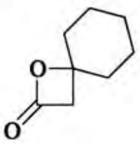
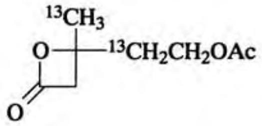
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn-Cu, Et_2O	 (87)	155
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 0°	 (—)	693
	$CH_2{=}C{=}O$	$ZnCl_2$, 0°	 (—)	716
	$CH_2{=}C{=}O$	$ZnCl_2$, $CHCl_3$	 (45)	713
	$CH_2{=}C{=}O$	BF_3•Et_2O, Et_2O, 0°	 (90.5)	719, 720
$^{13}CH_3CO^{13}CH_2CH_2OAc$	$CH_2{=}C{=}O$	BF_3•Et_2O, Et_2O, -30°	 (—)	721

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

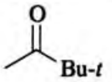
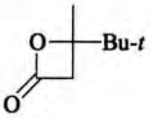
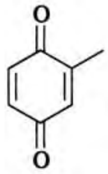
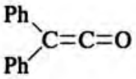
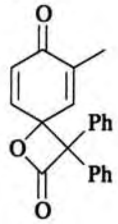
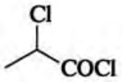
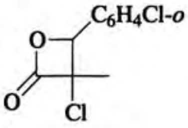
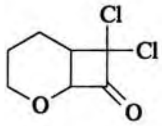
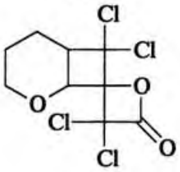
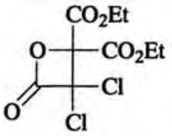
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	BF_3•Et_2O, CCl_4, 0°	 (67)	156
	 $Ph_2C{=}C{=}O$	Et_2O, pet. ether	 (28)	152
o-ClC_6H_4CHO		Et_3N, C_6H_{14}, rt	 (45)	151
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, rt	 (—)	693
$CO(CO_2Et)_2$	$Cl_2CHCOCl$	Et_3N, Et_2O, 0°	 (76)	324

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

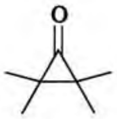
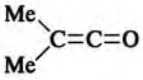
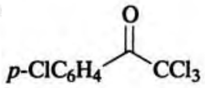
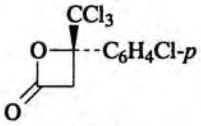
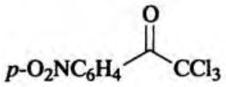
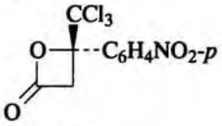
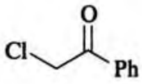
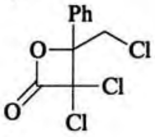
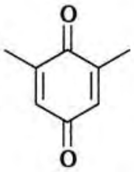
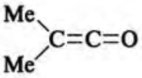
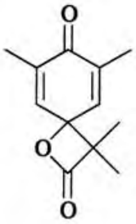
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C{=}C{=}O$	CH_2Cl_2, -78° 6 d	 (—)	157
C_8 	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (68) 90% ee	171
	$CH_2{=}C{=}O$	Quinidine, PhMe, -25°	 (95) 89% ee	171
	Cl_3CCOCl	Zn, Et_2O, rt	 (20)	151
	 $Me_2C{=}C{=}O$	THF, 0°	 (84)	165

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

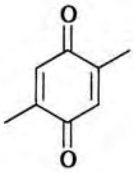
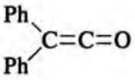
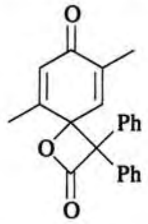
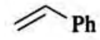
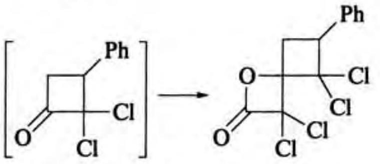
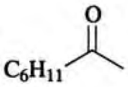
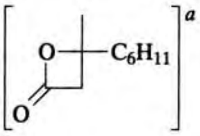
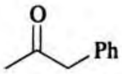
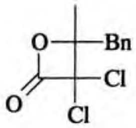
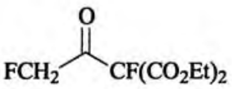
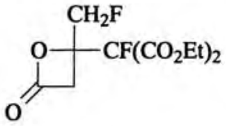
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	Et_2O, pet. ether	 (36)	152
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 0°	 (—)	693
	$CH_2{=}C{=}O$	BF_3•Et_2O, CCl_4, 0°	 (—)	156
	Cl_3CCOCl	Zn, Et_2O, rt	 (40)	151
	$CH_2{=}C{=}O$	$ZnCl_2$, Et_2O, 25°	 (24)	713

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

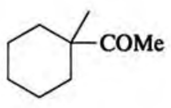
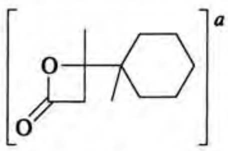
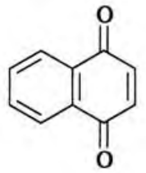
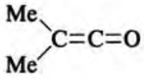
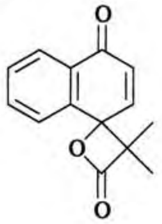
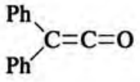
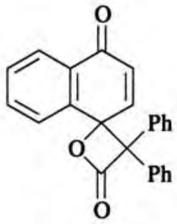
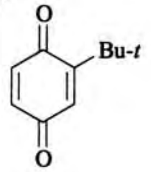
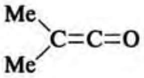
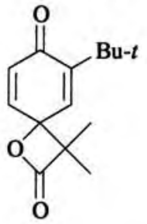
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	$BF_3•Et_2O$, CCl_4, 0°	 (—)	156
	 $Me_2C=C=O$	THF, 0°	 (70)	165
	 $Ph_2C=C=O$	Et_2O, pet. ether	 (43)	152
C_{10}				
	 $Me_2C=C=O$	THF, 0°	 (—)	165

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

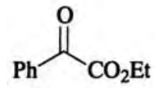
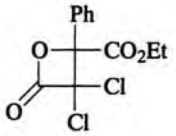
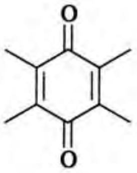
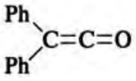
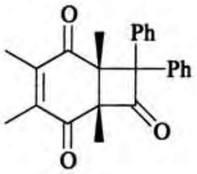
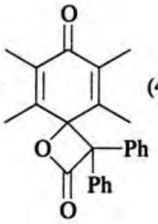
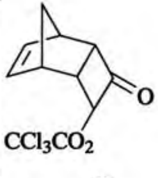
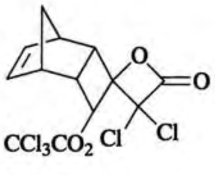
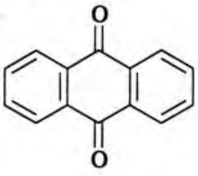
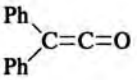
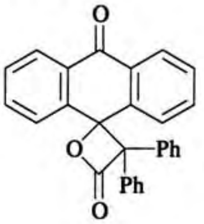
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, Et_2O, 10°	 (38)	692
	 $Ph_2C=C=O$	hν, C_6H_6	 (25) +  (49)	153
C_{11}				
	Cl_3CCOCl	Zn, Et_2O	 (16)	722
C_{14}				
	 $Ph_2C=C=O$	hν, C_6H_6	 (53)	153

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

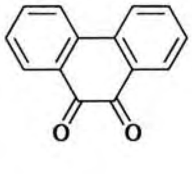
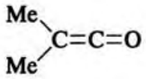
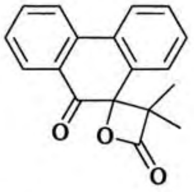
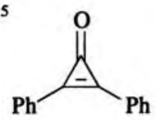
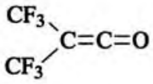
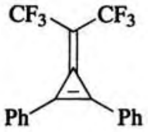
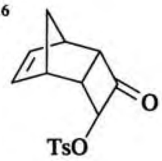
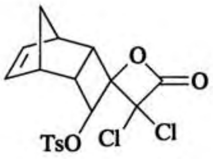
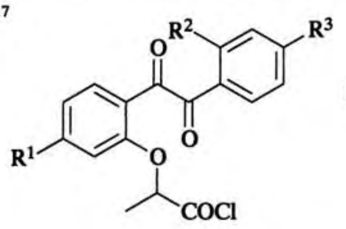
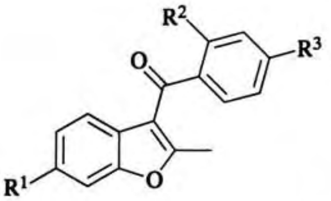
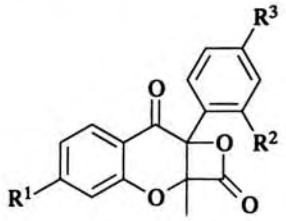
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Me_2C=C=O$	$ZnCl_2$, THF	 (62)	154
C_{15} 	 $(CF_3)_2C=C=O$	C_6H_6, 25°, 5 d	 (79)	723
C_{16} 	Cl_3CCOCl	Zn, Et_2O	 (26)	722

TABLE XIX. [2+2] CYCLOADDITION OF KETENES TO KETONES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17} 	Intramolecular	Et_3N, C_6H_6, 50°	 I +  II	724

R^1	R^2	R^3	I	II
H	H	H	(63)	(trace)
H	OMe	H	(24)	(49)
OMe	OMe	OMe	(0)	(57)

---

[a] The product was not isolated.

TABLE XX. [2+2] CYCLOADDITION OF KETENES TO THIOCARBONYL COMPOUNDS

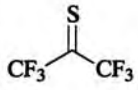
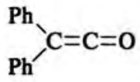
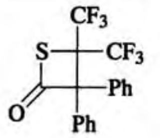
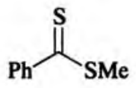
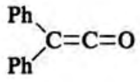
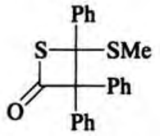
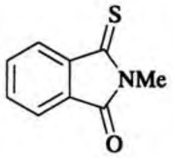
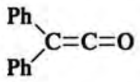
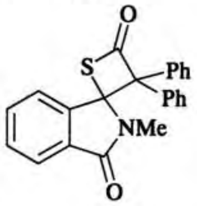
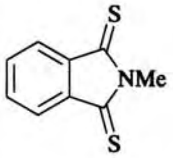
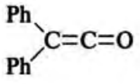
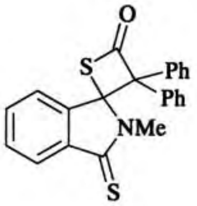
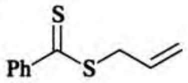
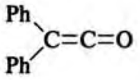
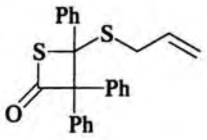
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3  $(CF_3)_2C=S$	 $Ph_2C=C=O$	KF, MeCN	 (59)	709
C_8  $PhC(=S)SMe$	 $Ph_2C=C=O$	—	 (61)	179
C_9 	 $Ph_2C=C=O$	hν, CH_2Cl_2, -60°	 (59)	177
	 $Ph_2C=C=O$	hν, CH_2Cl_2, -60°	 (42)	177
C_{10}  $PhC(=S)SCH_2CH=CH_2$	 $Ph_2C=C=O$	—	 (61)	179

TABLE XX. [2+2] CYCLOADDITION OF KETENES TO THIOCARBONYL COMPOUNDS (*Continued*)

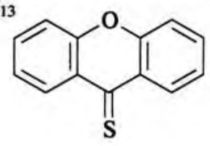
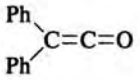
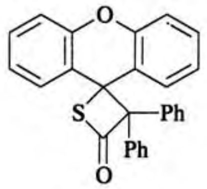
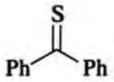
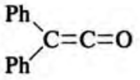
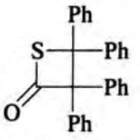
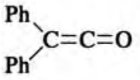
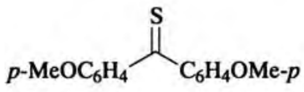
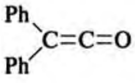
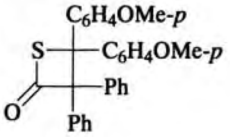
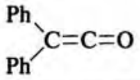
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{13} 	 $Ph_2C=C=O$	hν, CH_2Cl_2, -60°	 (100)	177
 $Ph_2C=S$	 $Ph_2C=C=O$	60°	 (74)	178
	 $Ph_2C=C=O$	Et_2O	" (80-90)	725
 $(p\text{-}MeOC_6H_4)_2C=S$	 $Ph_2C=C=O$	Et_2O	 (—)	725
	 $Ph_2C=C=O$	60°	" (34)	178

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS

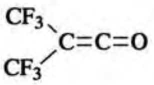
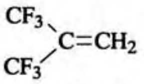
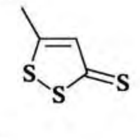
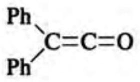
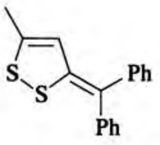
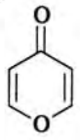
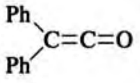
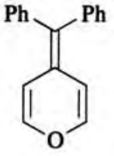
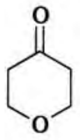
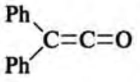
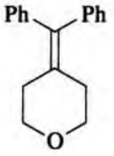
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2				
Cl_3CCHO	$MeCHClCOCl$	1. Et_3N 2. Pyrolysis, 2 mm	$CH_2{=}C{=}CHCCl_3$ (40-50)	726
	$EtCHClCOCl$	"	$MeCH{=}C{=}CHCCl_3$ (40-50)	726
	n-$PrCHClCOCl$	"	$EtCH{=}C{=}CHCCl_3$ (40-50)	726
C_3				
 $(CF_3)_2C{=}C{=}O$	$CH_2{=}C{=}O$	550°, 14 s	 $(CF_3)_2C{=}CH_2$ (26)	727
	$CH_2{=}C{=}O$	290-340°	" (82-100)	181
C_4				
	 $Ph_2C{=}C{=}O$	Xylene, 137°	 (10)	186
C_5				
	 $Ph_2C{=}C{=}O$	150°	 (50)	728
	 $Ph_2C{=}C{=}O$	—	 (29)	539, 729

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

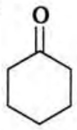
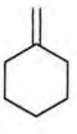
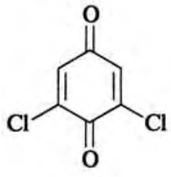
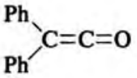
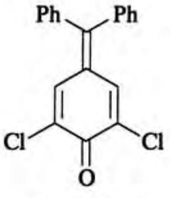
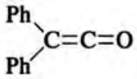
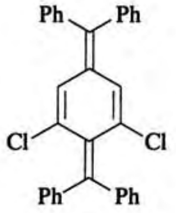
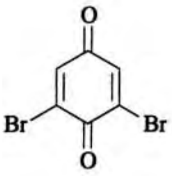
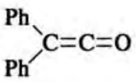
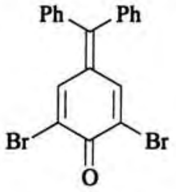
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
	$CH_2{=}C{=}O$	BF_3•Et_2O, 0-2°, 110°	 (60)	730
	 $Ph_2C{=}C{=}O$	100°, 24 h	 (—)	152
	 $Ph_2C{=}C{=}O$	130°, 1.5 h	 (—)	152
	 $Ph_2C{=}C{=}O$	Xylene, 140°	 (—)	152

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

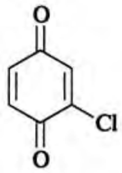
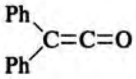
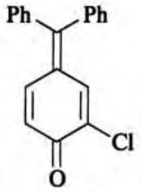
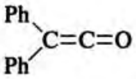
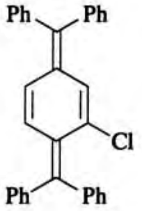
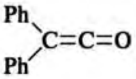
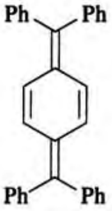
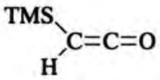
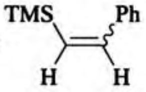
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	110°	 (—)	152
	 $Ph_2C=C=O$	120°	 (—)	152
	 $Ph_2C=C=O$	Xylene, 140°	 (—)	718
C_7				
PhCHO	BrF_2CCOCl	Zn, -10°	$PhCH=CF_2$ (11)	715
	 TMS(H)C=C=O	1. $BF_3 \cdot Et_2O$, -50° 2. 150-160°	 (75)	167

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

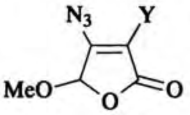
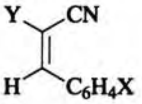
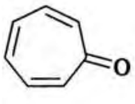
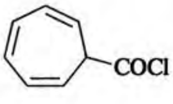
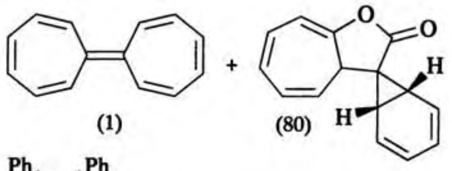
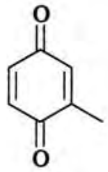
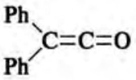
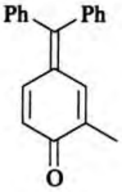
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
XC_6H_4CHO		C_6H_6, 80°, 5 h		182
X	Y			
p-Cl	Cl		(32)	
p-Cl	Br		(27)	
p-O_2N	Cl		(8)	
p-O_2N	Br		(<5)	
H	Cl		(61)	
H	Br		(48)	
p-Me	Cl		(54)	
p-MeO	Cl		(73)	
p-MeO	Br		(79)	
2,4-$(MeO)_2$	Cl		(92)	
p-NMe_2	Cl		(78)	
p-MeO_2C	Cl		(61)	
p-MeO_2C	Br		(51)	
		Et_3N	 (1) + (80)	187
	 $Ph_2C=C=O$	110°	 (—)	152

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

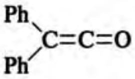
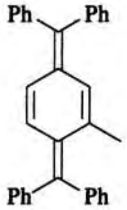
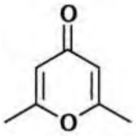
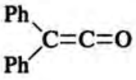
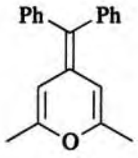
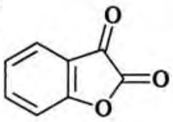
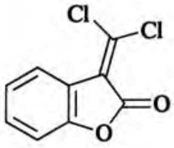
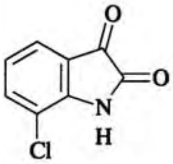
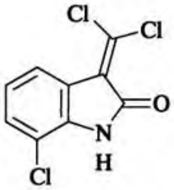
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	—	 (—)	152
	 $Ph_2C{=}C{=}O$	150°	 (73)	728
C_8 	$Cl_2CHCOCl$	Et_3N, Et_2O	 (61)	324
	$Cl_2CHCOCl$	Et_3N, $CHCl_3$, 20°	 (61)	324, 692

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL A ND THIOCARBONYL COMPOUNDS (*Continued*)

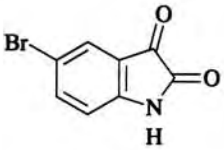
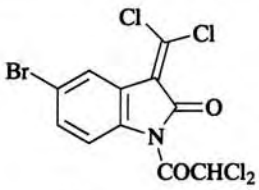
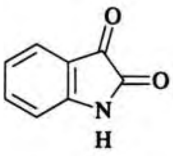
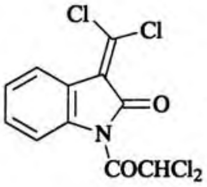
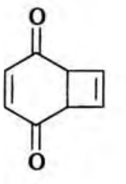
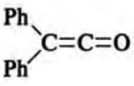
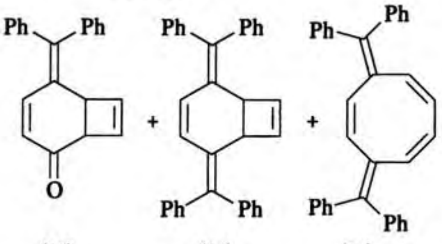
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, $CHCl_3$, 20°	 (67)	324, 692
	$Cl_2CHCOCl$	Et_3N, $CHCl_3$, 20°	 (80)	324, 692
	$Br_2CHCOBr$	Et_3N, $CHCl_3$, 20°	 (44)	324, 692
	 $Ph_2C{=}C{=}O$	PhMe, 111°	 (35) (24) (12)	731

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

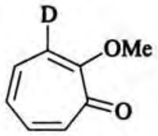
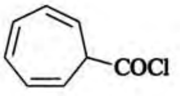
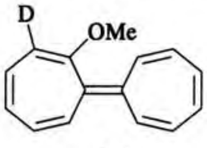
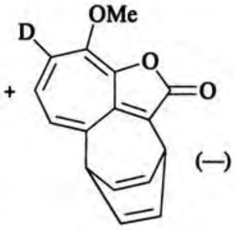
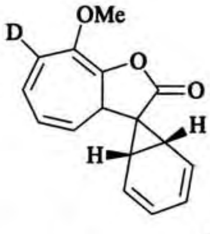
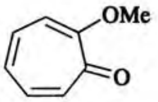
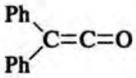
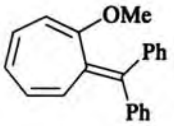
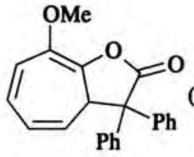
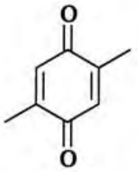
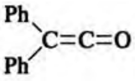
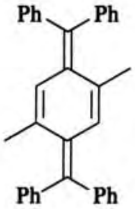
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Et_3N, C_6H_{14}	 (—) +  (—) +  (—)	732
	 $Ph_2C=C=O$	C_6H_6, 80°	 (7) +  (60)	733
	 $Ph_2C=C=O$	Xylene, 140°	 (—)	718

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

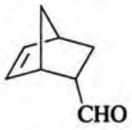
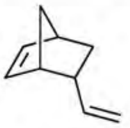
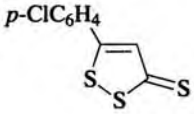
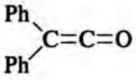
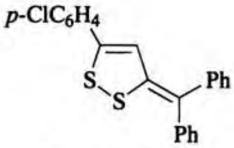
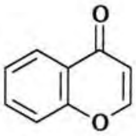
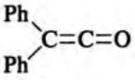
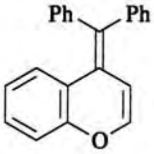
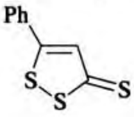
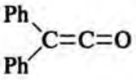
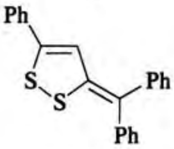
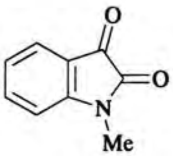
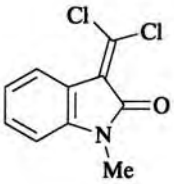
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	1. rt 2. 170-190°	 (94)	180
C_9				
	 $Ph_2C=C=O$	Xylene, 137°	 (75)	186
	 $Ph_2C=C=O$	150°	 (65)	728
	 $Ph_2C=C=O$	Xylene, 137°	 (80)	186
	$Cl_2CHCOCl$	Et_3N, $CHCl_3$, 20°	 (69)	734

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

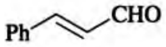
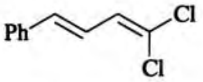
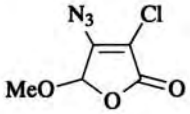
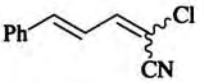
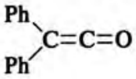
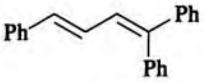
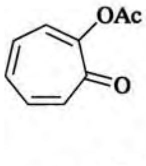
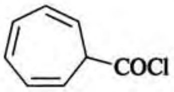
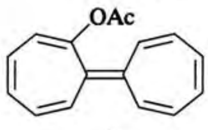
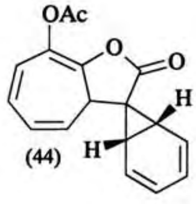
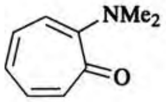
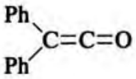
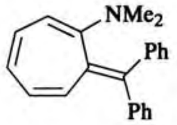
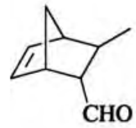
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cl_3CCOCl	Zn, Et_2O	 (35)	698
		C_6H_6, 80°	 (85)	23
	 $Ph_2C{=}C{=}O$	$BF_3{\bullet}Et_2O$, Et_2O	 (52)	698
		Et_3N	 (9) +  (44)	735
	 $Ph_2C{=}C{=}O$	C_6H_6, 80°	 (8)	733
	$CH_2{=}C{=}O$	—	 (85)	736

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

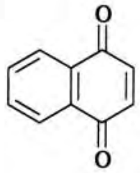
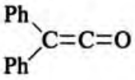
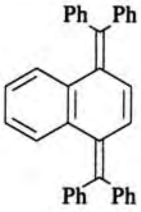
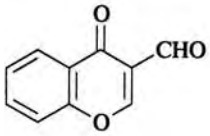
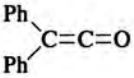
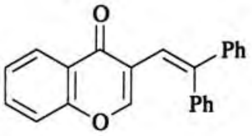
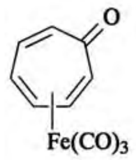
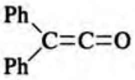
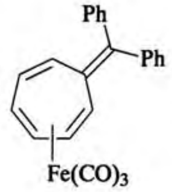
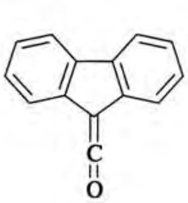
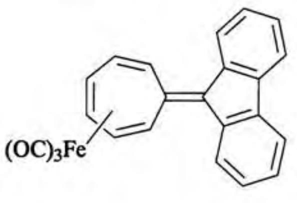
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	PhMe, 100°	 (—)	152, 718
	 $Ph_2C{=}C{=}O$	180-200°	 (30)	256
	 $Ph_2C{=}C{=}O$	C_6H_6, 25°	 (20)	737
		C_6H_{12}, 25°	 (—)	737

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

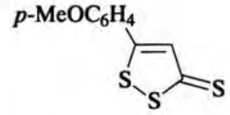
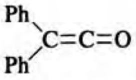
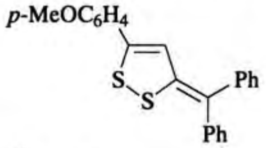
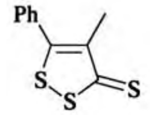
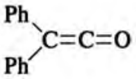
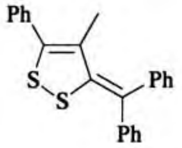
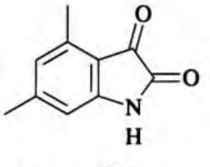
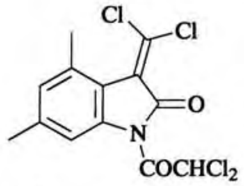
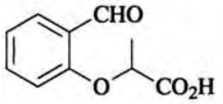
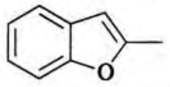
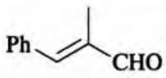
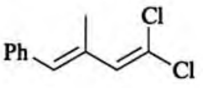
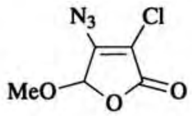
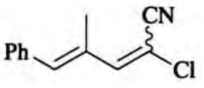
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	Xylene, 137°	 (40)	186
	 $Ph_2C{=}C{=}O$	Xylene, 137°	 (60)	186
	$Cl_2CHCOCl$	Et_3N, $CHCl_3$, 20°	 (38)	324, 692
	—	1. $(COCl)_2$ 2. Et_3N, C_6H_6, 80°	 (57)	185, 534
	Cl_3CCOCl	Zn, Et_2O	 (32)	698
		C_6H_6, 80°	 (79)	23

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

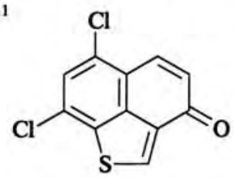
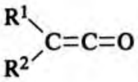
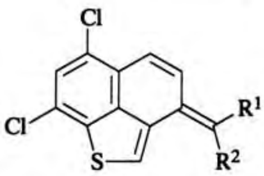
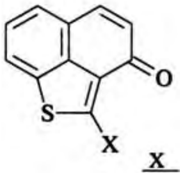
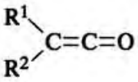
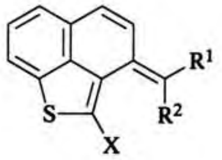
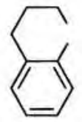
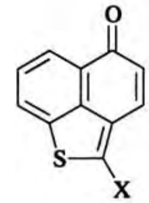
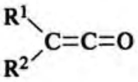
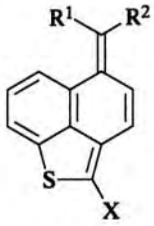
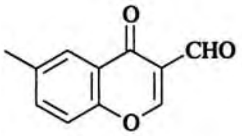
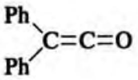
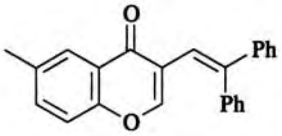
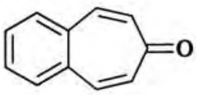
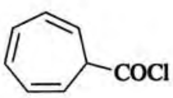
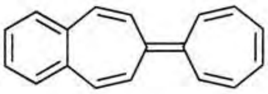
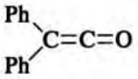
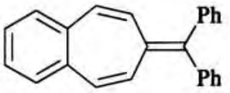
Reactant	Ketene or Ketene Source		Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	 $R^1R^2C{=}C{=}O$		C_6H_6, 80°		184
	R^1	R^2			
	Me	CN		(34)	
	t-Bu	CN		(72)	
	Ph	CN		(42)	
	Ph	Me		(21)	
	Ph	Ph		(33)	
	Ph	2,4,6-$Me_3C_6H_2$		(54)	
	Ph	1-$C_{10}H_7$		(74)	
	 $R^1R^2C{=}C{=}O$		C_6H_6, 80°		325
X	R^1	R^2			
H	Ph	Ph		(35)	
Me	Me	CN		(37)	
Me	*t*-Bu	CN		(75)	
Me				(47)	
Me	Ph	Ph		(56)	
Me	9-Fluorenylidene			(61)	

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $R^1R^2C{=}C{=}O$	C_6H_6, 80°		
	 $Ph_2C{=}C{=}O$	180-200°	 (27)	256
		Et_3N	 (50)	187
	 $Ph_2C{=}C{=}O$	121°	 (69)	539, 738

X	R^1	R^2	Product(s) and Yield(s) (%)	Refs.
Br	*t*-Bu	CN	(49)	325
Br	Ph	Ph	(43)	325
H	Me	CN	(34)	184
H	Ph	CN	(42)	184
H	Ph	Ph	(30)	184
H	Ph	2,4,6-$Me_3C_6H_2$	(3)	184
H	Ph	1-$C_{10}H_7$	(63)	184

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

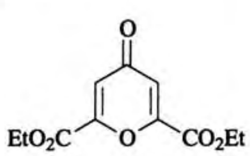
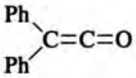
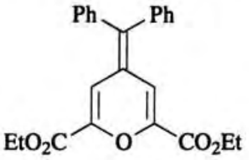
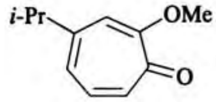
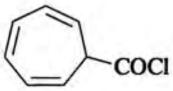
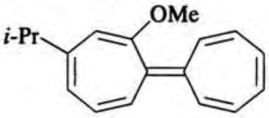
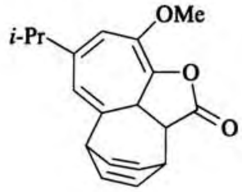
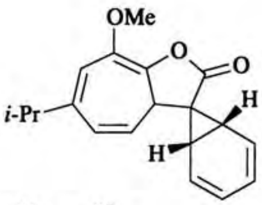
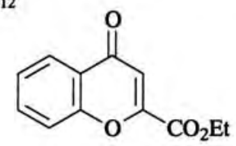
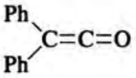
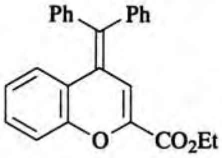
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	150°	 (81)	728
		Et_3N, C_6H_{14}	 (24) +  (24) +  (15)	732
C_{12} 	 $Ph_2C{=}C{=}O$	150°	 (94)	728

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

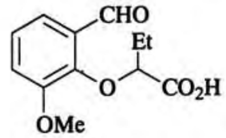
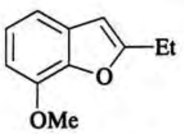
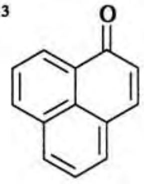
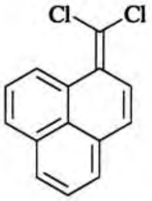
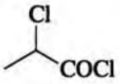
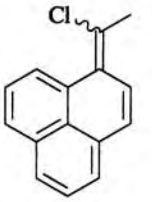
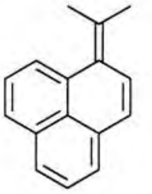
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	—	(COCl)$_2$, C$_6$H$_6$, Et$_3$N, 80°	 (53)	185, 534
C$_{13}$ 	Cl$_2$CHCOCl	C$_6$H$_6$, Et$_3$N	 (>80)	739
		C$_6$H$_6$, Et$_3$N	 (>80)	739
	i-PrCOCl	C$_6$H$_6$, Et$_3$N	 (>80)	739

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

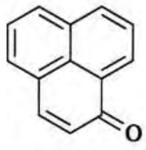
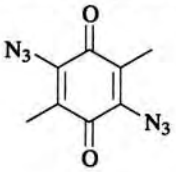
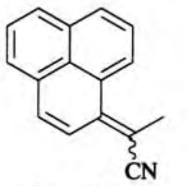
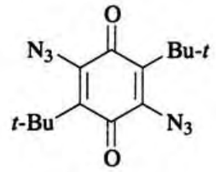
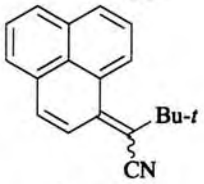
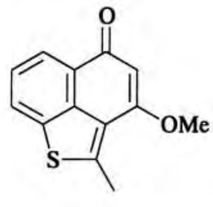
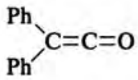
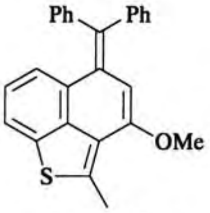
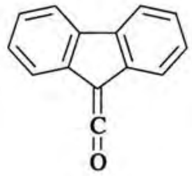
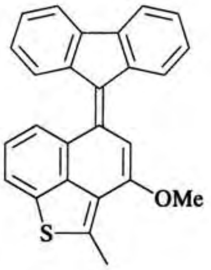
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C$_6$H$_6$, 80°	 (69)	325
		C$_6$H$_6$, 80°	 (75)	325
		C$_6$H$_6$, 66°	 (52)	740
		45°, 1 h	 (64)	740

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

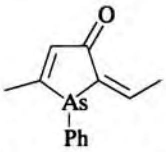
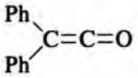
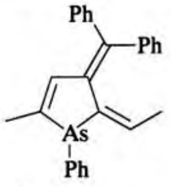
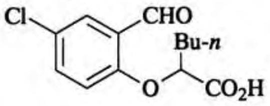
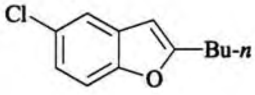
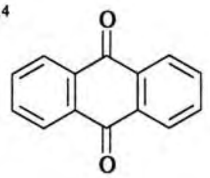
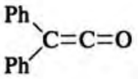
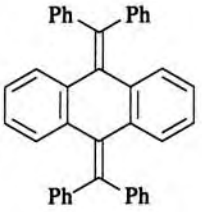
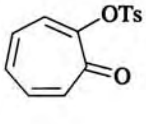
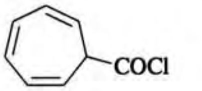
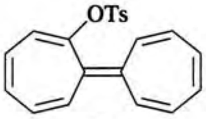
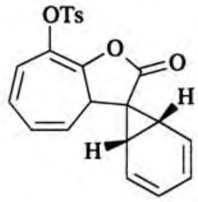
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	150-200°	 (34)	741
	—	TsCl, C_6H_6, Et_3N, 80°	 (72)	185
C_{14} 	 $Ph_2C=C=O$	Xylene, 140°	 (—)	718
		Et_3N	 (10) +  (49)	735

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

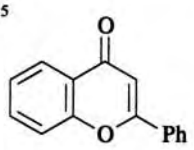
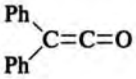
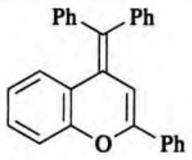
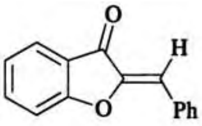
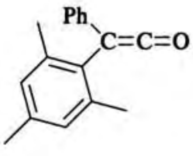
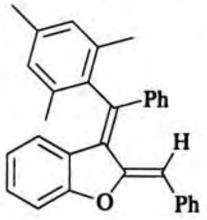
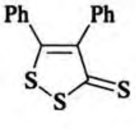
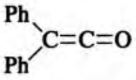
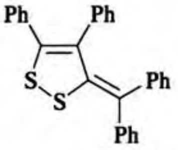
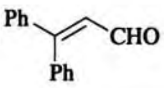
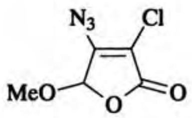
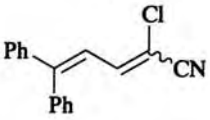
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 	 $Ph_2C=C=O$	150°	 (70)	728
		140°, 4 h	 (42)	742
	 $Ph_2C=C=O$	Xylene, 137°	 (35)	186
		—	 (82)	23

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

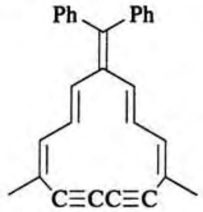
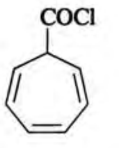
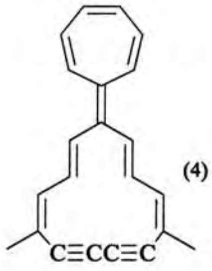
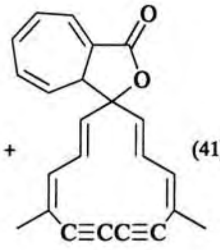
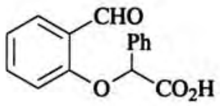
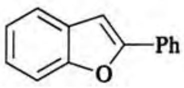
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ph_2CHCOCl$	Et_3N, Et_2O	 (32)	743, 744
		Et_3N, C_6H_6, 80°	 (4) +  (41)	745
	—	1. $(COCl)_2$ 2. Et_3N, C_6H_6, 80°	 (75)	185, 534

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

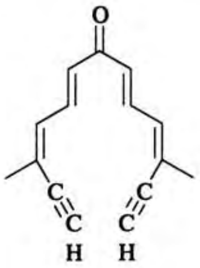
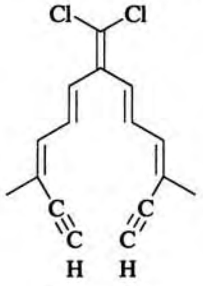
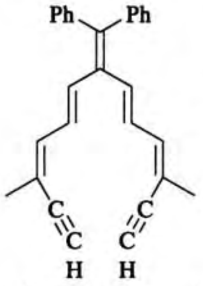
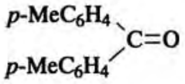
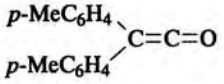
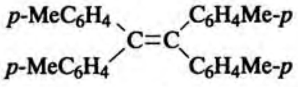
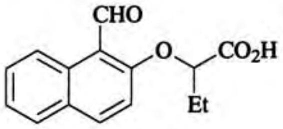
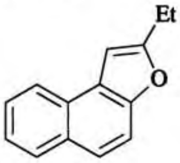
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°, 3-5 h	 (15)	746
	$Ph_2CHCOCl$	Et_3N, Et_2O	 (36)	743, 744
 $(p\text{-}MeC_6H_4)_2C{=}O$	 $(p\text{-}MeC_6H_4)_2C{=}C{=}O$	—	 $(p\text{-}MeC_6H_4)_2C{=}C(C_6H_4Me\text{-}p)_2$ (—)	747
	—	TsCl, C_6H_6, Et_3N, 80°	 (74)	185

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

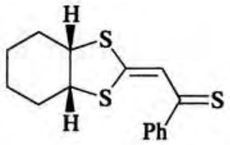
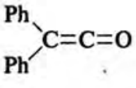
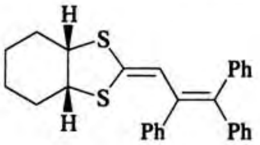
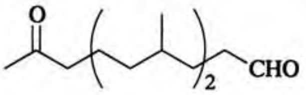
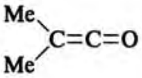
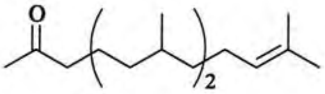
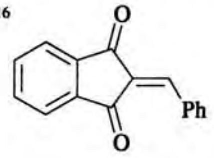
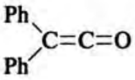
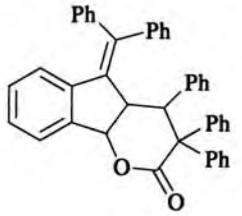
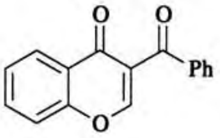
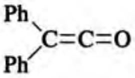
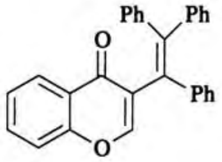
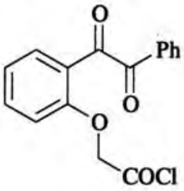
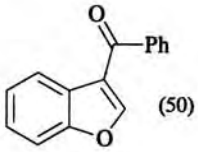
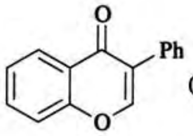
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		DMF, 25°	 (88)	270
		1. BF_3•Et_2O, *i*-PrOAc, 85° 2. 150°, 2 h	 (82)	162
C_{16} 		160°	 (21)	748
		190-250°, 4 h	 (—)	749
	—	Et_3N, C_6H_6, 50°	 (50) +  (23)	724

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

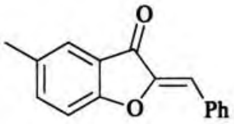
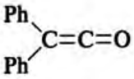
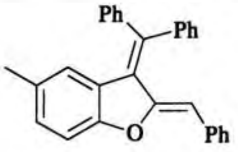
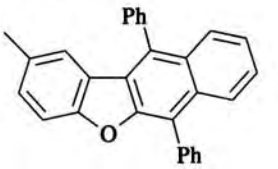
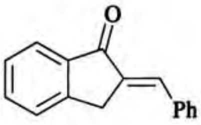
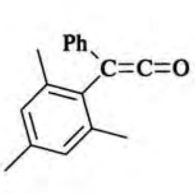
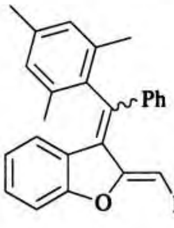
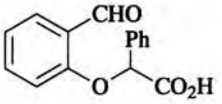
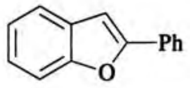
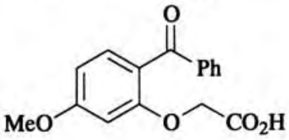
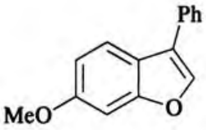
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		56°	 (—) +  (—)	750
		140°, 4 h	 (low)	751
	—	1. $(COCl)_2$ 2. Et_3N, C_6H_6, 80°	 (78)	185, 534
	—	1. $(COCl)_2$ 2. Et_3N, C_6H_6, 80°	 (74)	185, 534

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

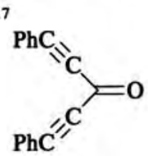
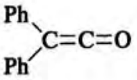
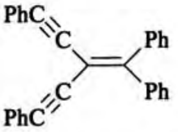
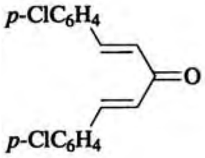
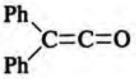
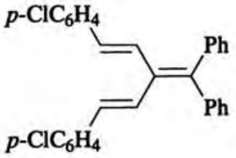
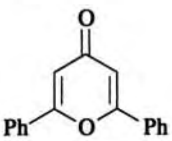
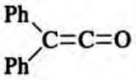
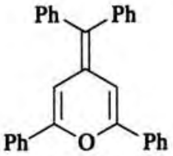
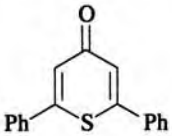
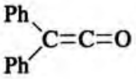
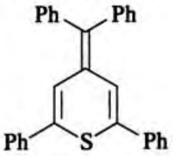
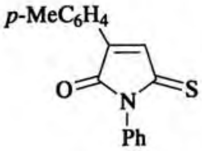
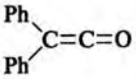
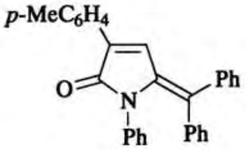
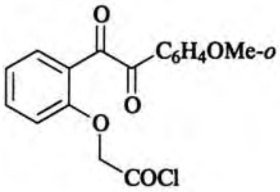
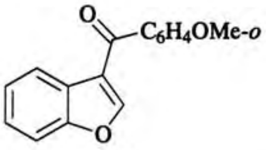
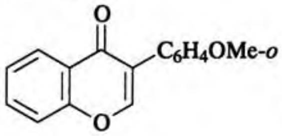
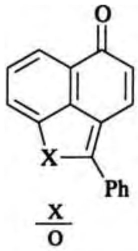
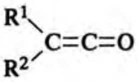
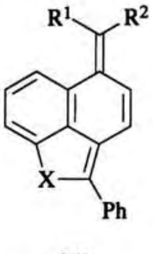
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{17}				
	 $Ph_2C=C=O$	130°	 (18)	741
	 $Ph_2C=C=O$	PhMe, 111°	 (—)	752
	 $Ph_2C=C=O$	150°	 (75)	728
	 $Ph_2C=C=O$	150°	 (90)	728
	 $Ph_2C=C=O$	PhMe, 111°	 (53)	753

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	—	Et_3N, C_6H_6, 50°	 (15) +  (55)	724
	 $R^1R^2C=C=O$	C_6H_6, rt to 80°		

X	R^1	R^2		
O	CN	CN	(40)	754
O	Me	CN	(45)	754
O	*t*-Bu	CN	(51)	754
S	*t*-Bu	CN	(64)	325
O	Ph	CN	(40)	754
O	Ph	Ph	(76)	754
S	Ph	Ph	(84)	755, 756
S	9-Fluorenylidene		(38)	756
O	Ph	$1\text{-}C_{10}H_7$	(57)	754

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

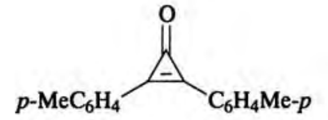
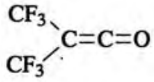
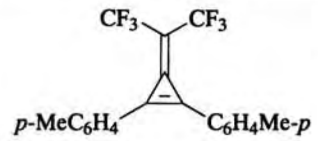
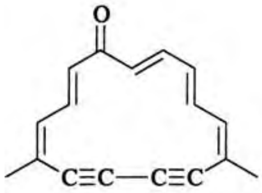
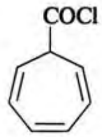
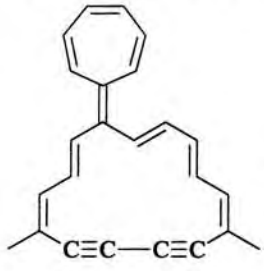
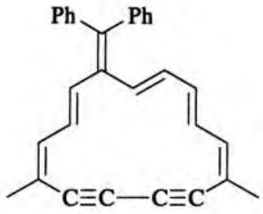
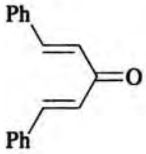
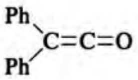
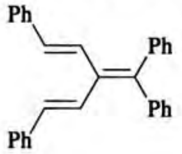
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(CF_3)_2C=C=O$	PhMe, rt, 5 d	 (59)	757
		Et_3N, C_6H_6, 80°	 (30)	183
	$Ph_2CHCOCl$	Et_3N, Et_2O	 (51)	743, 744
	 $Ph_2C=C=O$	PhMe, 111°	 (62)	752

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

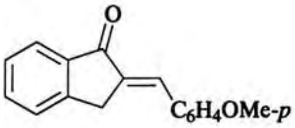
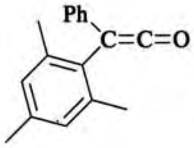
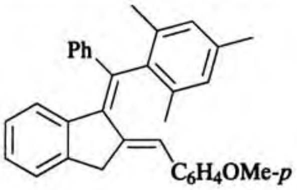
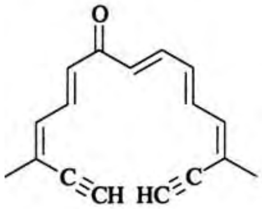
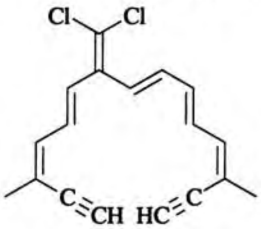
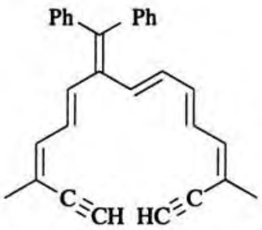
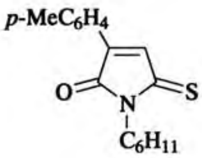
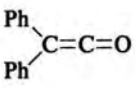
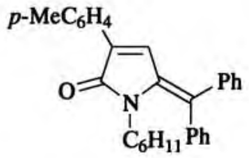
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		140°	 (—)	751
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°, 35 h	 (12)	746
	$Ph_2CHCOCl$	Et_3N, Et_2O	 (35)	743, 744
	 $Ph_2C=C=O$	PhMe, 111°	 (66)	753

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

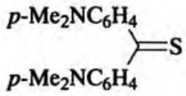
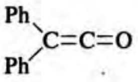
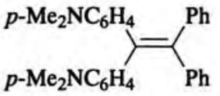
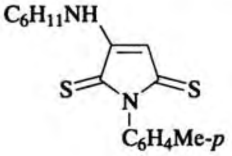
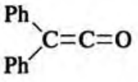
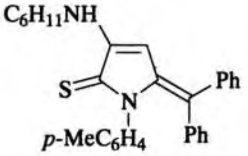
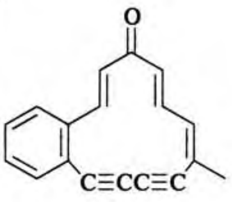
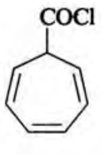
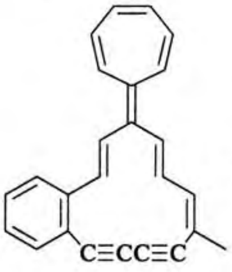
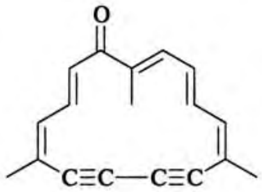
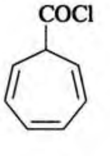
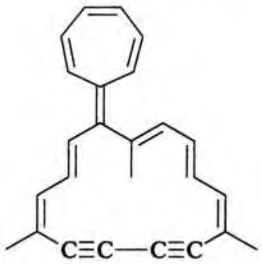
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
 $(p\text{-}Me_2NC_6H_4)_2C{=}S$	 $Ph_2C{=}C{=}O$	Et_2O	 $(p\text{-}Me_2NC_6H_4)_2C{=}CPh_2$ (—)	725
	 $Ph_2C{=}C{=}O$	PhMe, 111°	 (61)	753
C_{18}				
		Et_3N, C_6H_6, 80°	 (67)	183
		Et_3N, C_6H_6, 80°	 (86)	183

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

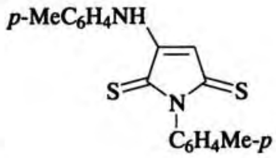
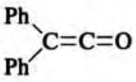
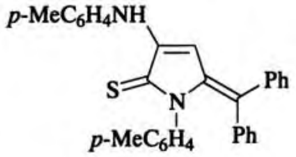
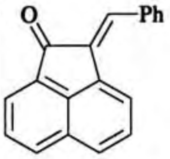
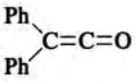
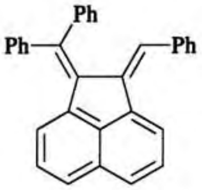
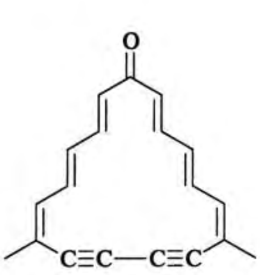
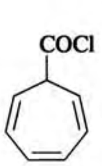
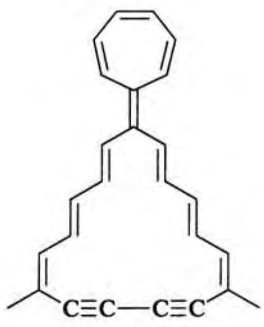
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	PhMe, 111°	 (65)	753
C_{19}				
	 $Ph_2C{=}C{=}O$	130°, 2 h	 (—)[a]	254
		Et_3N, C_6H_6, 80°	 (52)	183

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

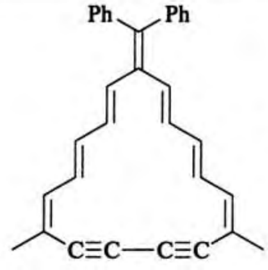
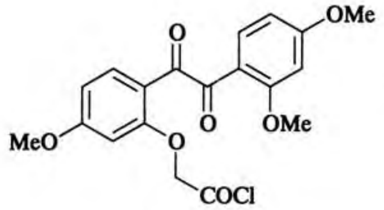
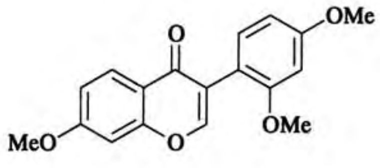
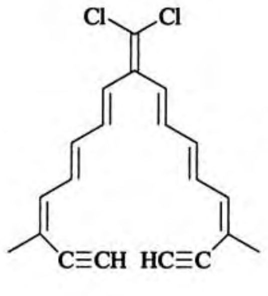
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ph_2CHCOCl$	Et_3N, C_6H_6	 (58)	743, 744
	—	Et_3N, C_6H_6, 50°	 (59)	724
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°, 3-5 h	 (11)	746

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

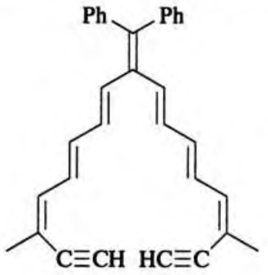
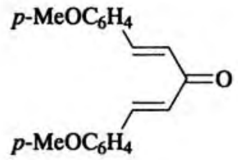
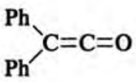
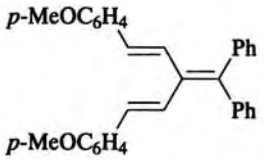
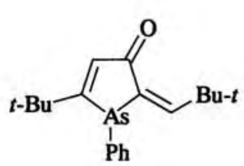
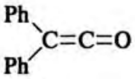
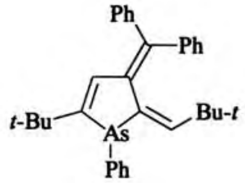
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ph_2CHCOCl$	Et_3N, Et_2O	 (22)	743, 744
	 $Ph_2C{=}C{=}O$	PhMe, 111°	 (—)	752
	 $Ph_2C{=}C{=}O$	150-200°	 (—)	741

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

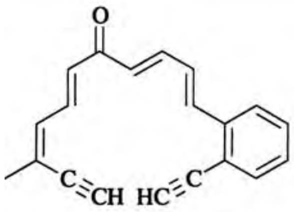
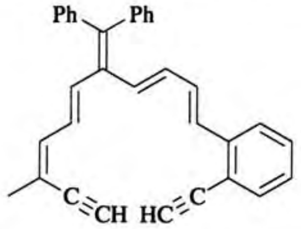
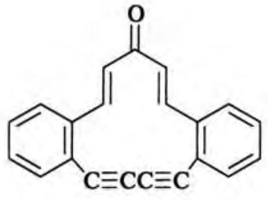
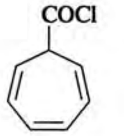
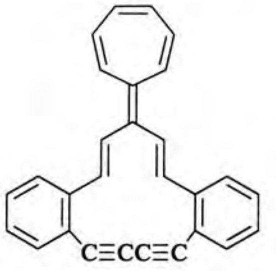
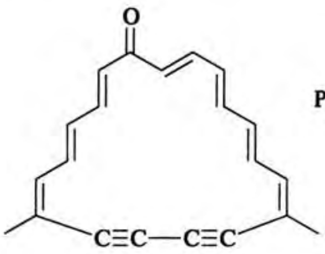
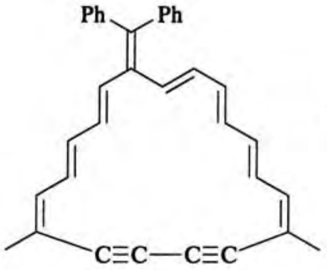
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Ph_2CHCOCl$	Et_3N, Et_2O		(34)	743, 758
		Et_3N, C_6H_6, 80°		(24)	745
	$Ph_2CHCOCl$	Et_3N, Et_2O		(35)	743, 744

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

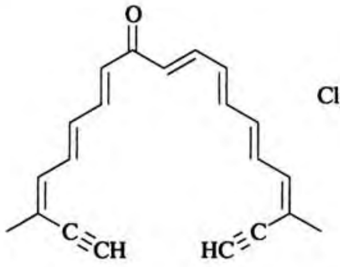
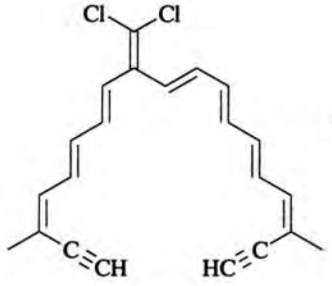
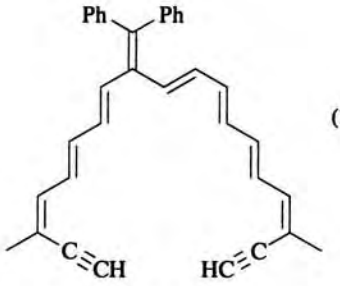
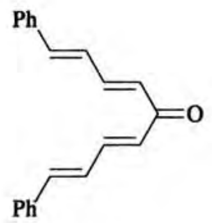
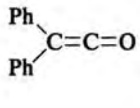
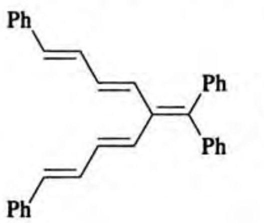
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°, 3-5 h		(14)	746
	$Ph_2CHCOCl$	Et_3N, Et_2O		(18)	743, 744
	 $Ph_2C{=}C{=}O$	PhMe, 111°		(—)	752

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

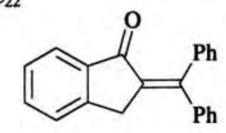
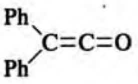
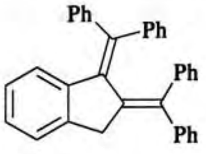
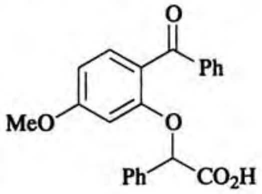
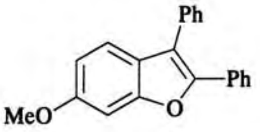
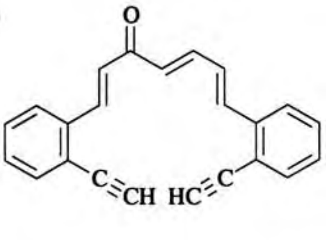
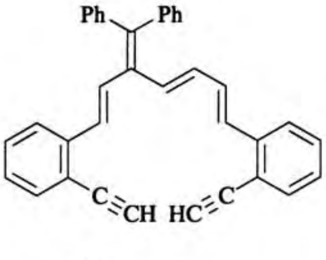
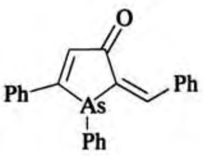
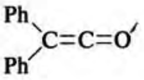
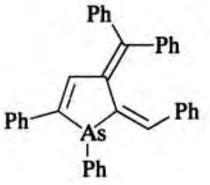
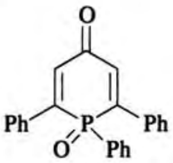
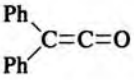
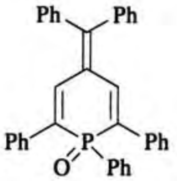
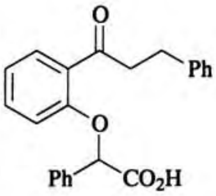
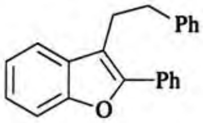
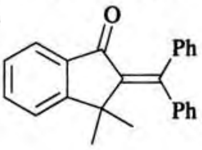
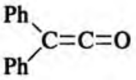
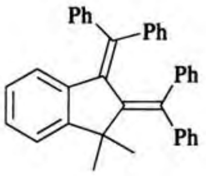
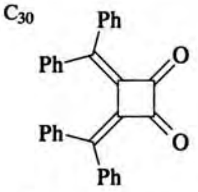
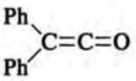
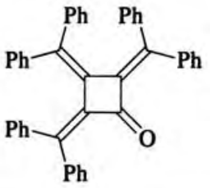
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	 $Ph_2C=C=O$	160°, 6 h	 (72)	759
	—	1. $(COCl)_2$ 2. Et_3N, C_6H_6, 80°	 (82)	185, 534
C_{23} 	$Ph_2CHCOCl$	Et_3N, Et_2O	 (54)	743, 758
	 $Ph_2C=C=O$	150-200°	 (69)	741

TABLE XXI. OLEFINS FROM REACTION OF KETENES WITH CARBONYL AND THIOCARBONYL COMPOUNDS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	170°	 (80)	760
	—	TsCl, C_6H_6, Et_3N, 80°	 (89)	185
C_{24} 	 $Ph_2C=C=O$	160°, 1 h	 (53)	759
C_{30} 	 $Ph_2C=C=O$	Xylene, 137°	 (45)	761

---

[a] The product could not be isolated.

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES

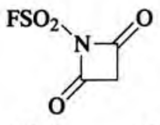
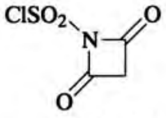
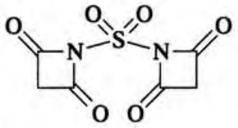
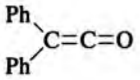
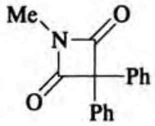
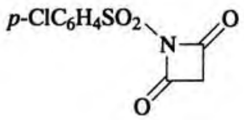
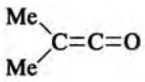
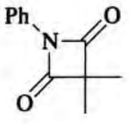
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1				
FSO_2NCO	$CH_2{=}C{=}O$	$CHCl_3$, -50°	 (61)	190, 189
$ClSO_2NCO$	$CH_2{=}C{=}O$	$CHCl_3$, -50°	 (54)	190, 189
C_2				
$SO_2(NCO)_2$	$CH_2{=}C{=}O$	Me_2CO, -20°	 (74)	190, 762
MeNCO	 $Ph_2C{=}C{=}O$	220°, 5 h	 (18)	763
C_7				
p-$ClC_6H_4SO_2NCO$	$CH_2{=}C{=}O$	$CHCl_3$, -30°	 (47)	189, 190
PhNCO	 $Me_2C{=}C{=}O$	MeCN, 82°	 (30)	188

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES (*Continued*)

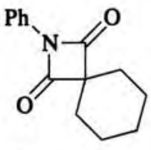
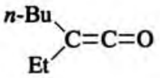
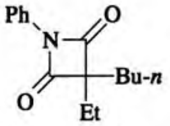
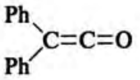
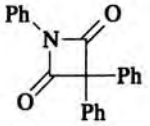
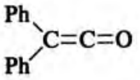
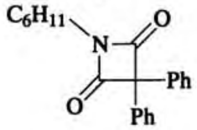
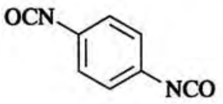
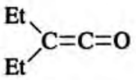
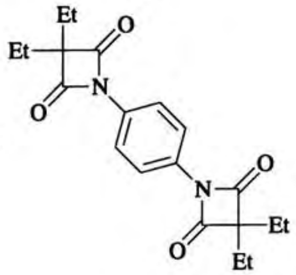
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$C_6H_{11}COCl$	Et_3N, C_6H_6	 (50)	764
	 $n\text{-}Bu(Et)C{=}C{=}O$	180°, 5 h	 (70)	188
	 $Ph_2C{=}C{=}O$	150°, 15 h	 (20)	765, 766
$C_6H_{11}NCO$	 $Ph_2C{=}C{=}O$	220°, 5 h	 (26)	763
C_8				
	 $Et_2C{=}C{=}O$	PhMe, 180°, 5 h	 (91)	188

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES (*Continued*)

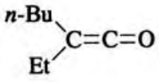
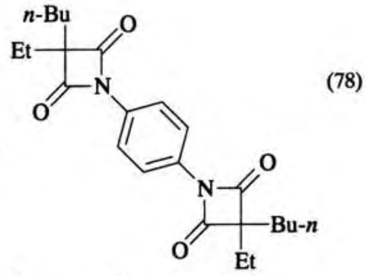
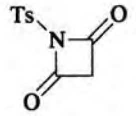
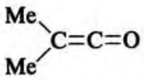
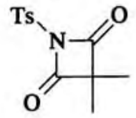
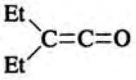
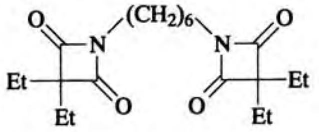
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $n\text{-Bu(Et)C=C=O}$	PhMe, 180°, 5 h	 (78)	188
TsNCO	$CH_2=C=O$	MeCN	 (54)	188
	$CH_2=C=O$	CH_2Cl_2, -10°	" (42)	190
	$CH_2=C=O$	$CHCl_3$, -30°	" (42)	189, 766, 767
	 $Me_2C=C=O$	C_6H_6, 10-20°	 (94)	188
$OCN(CH_2)_2NCO$	 $Et_2C=C=O$	PhMe, 180°	 (30)	188

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES (*Continued*)

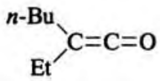
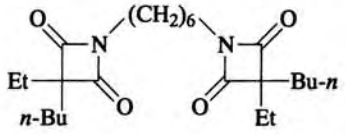
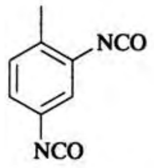
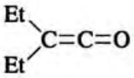
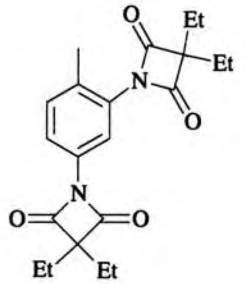
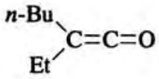
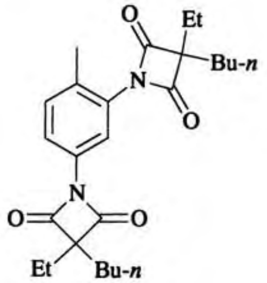
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $n\text{-Bu(Et)C=C=O}$	PhMe, 180°	 (10)	188
C_9 	 $Et_2C=C=O$	PhMe, 180°	 (85)	188
	 $n\text{-Bu(Et)C=C=O}$	PhMe, 180°	 (80)	188

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES (*Continued*)

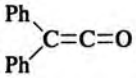
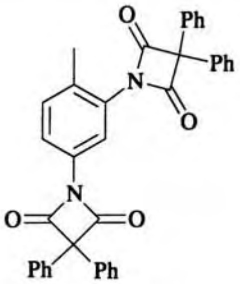
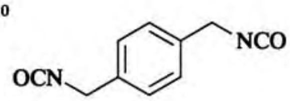
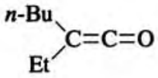
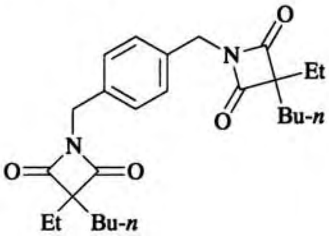
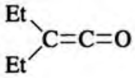
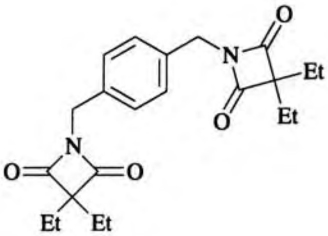
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	PhMe, 180°	 (30)	188
C_{10} 	 $(n\text{-}Bu)(Et)C=C=O$	PhMe, 180°	 (75)	188
	 $Et_2C=C=O$	PhMe, 180°	 (50)	188

TABLE XXII. [2+2] CYCLOADDITION OF KETENES TO ISOCYANATES (*Continued*)

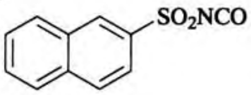
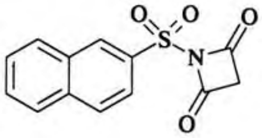
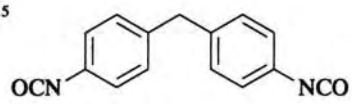
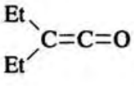
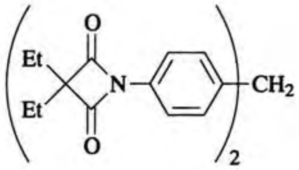
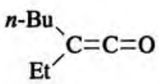
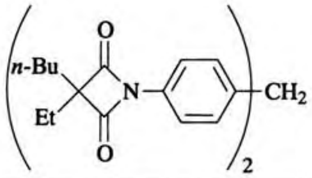
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 	$CH_2=C=O$	EtOAc, 0°	 (50)	189
C_{15} 	 $Et_2C=C=O$	PhMe, 180°	 (80)	188
	 $(n\text{-}Bu)(Et)C=C=O$	PhMe, 180°	 (65)	188

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES

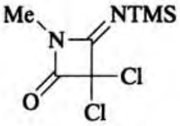
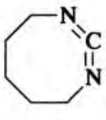
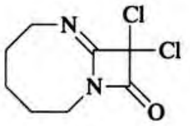
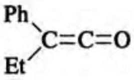
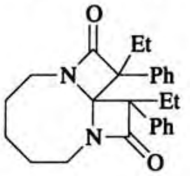
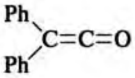
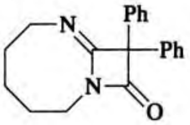
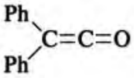
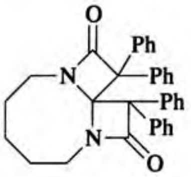
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_5				
TMSN=C=NMe	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 50°	 (35)	768
C_6 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 50°	 (60-80)	192
	 $\mathrm{Ph(Et)C{=}C{=}O}$	Et_2O, 25°, xs ketene	 (91)	192
	 $\mathrm{Ph_2C{=}C{=}O}$	Et_2O, 25°	 (90)	192
	 $\mathrm{Ph_2C{=}C{=}O}$	Et_2O, 25°, xs ketene	 (91)	192

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

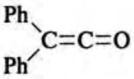
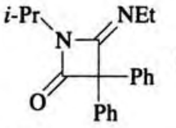
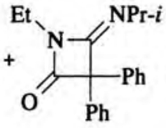
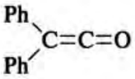
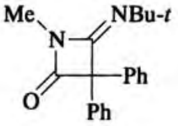
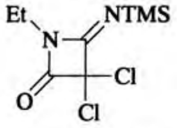
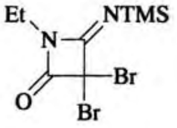
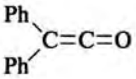
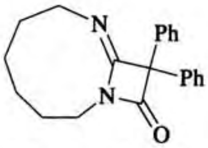
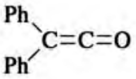
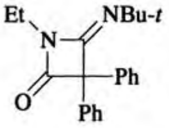
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
EtN=C=NPr-*i*	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (15) +  (15)	769
MeN=C=NBu-*t*	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (70)	769
TMSN=C=NEt	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 50°	 (37)	768
	$Br_2CHCOCl$	Et_3N, C_6H_{14}, 50°	 (15)	768
C_7 	 $\mathrm{Ph_2C{=}C{=}O}$	Et_2O, 25°	 (90)	192
EtN=C=NBu-*t*	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (71)	769

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

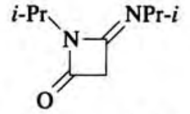
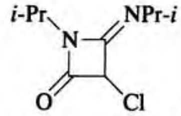
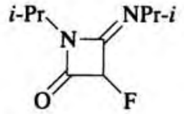
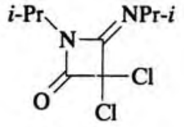
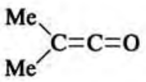
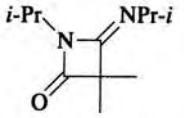
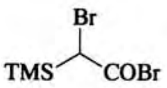
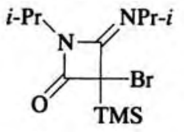
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
i-PrN=C=NPr-*i*	$CH_2=C=O$	rt		(5)	770
	$ClCH_2COCl$	Et_3N, C_6H_{14}, 69°		(20)	770
	FCH_2COCl	Et_3N, Et_2O, -78°		(40)	770
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 50°		(42)	768
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 81°	" (53)		771
	 $Me_2C=C=O$	C_6H_{14}, 69°, 8 h		(32)	770
		Et_3N, C_7H_{16}, 98°		(90)	772

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

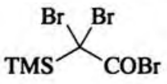
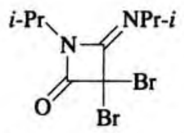
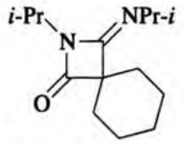
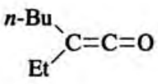
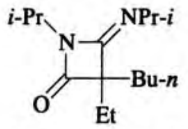
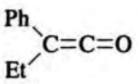
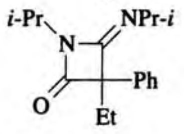
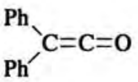
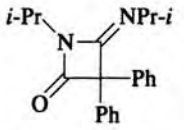
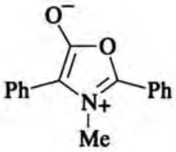
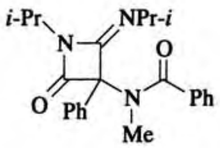
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
		Et_3N, CCl_4		(30)	771
	$C_6H_{11}COCl$	Et_3N, C_6H_6		(51)	527
	 $(n\text{-}Bu)(Et)C=C=O$	C_6H_{14}, 69°		(12)	770
	 $(Ph)(Et)C=C=O$	C_6H_6, rt		(57)	770
	 $Ph_2C=C=O$	C_6H_6, rt		(80-88)	769, 770 773, 774
		80°		(63)	775, 776

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

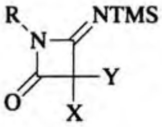
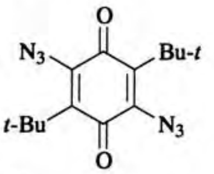
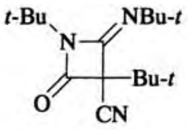
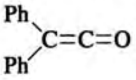
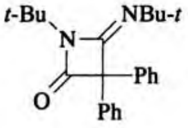
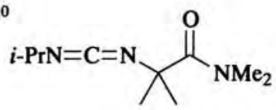
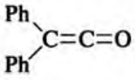
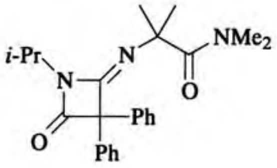
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
TMSN=C=NR	XYCHCOCl	Et_3N, C_6H_{14}, 50°		768
R	X Y			
n-Bu	Cl Cl		(36)	
i-Bu	Cl Cl		(40)	
t-Bu	Cl Cl		(45)	
t-Bu	Br Br		(28)	
t-Bu	Cl Me		(23)	
C_9				
t-BuN=C=NBu-*t*		C_6H_6, 80°	 (88)	191
	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (75)	769
C_{10}				
	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (59)	193

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

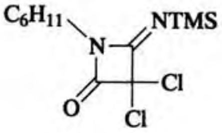
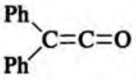
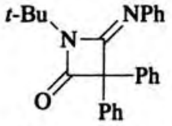
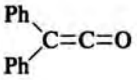
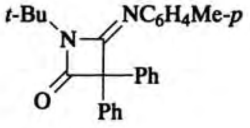
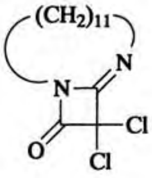
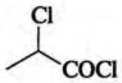
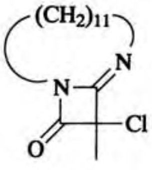
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$TMSN{=}C{=}NC_6H_{11}$	$Cl_2CHCOCl$	Et_3N, C_6H_{14}, 50°	 (28)	768
t-BuN=C=NPh	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (22)	769
t-BuN=C=NC_6H_4Me-*p*	 $\mathrm{Ph_2C{=}C{=}O}$	C_6H_6, 25°	 (30)	769
	$Cl_2CHCOCl$	Et_3N, C_6H_{14}	 (60-80)	192
		Et_3N, C_6H_{14}	 (60-80)	192

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

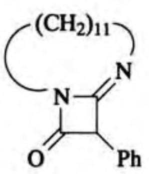
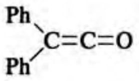
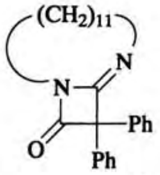
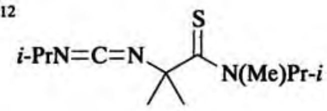
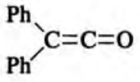
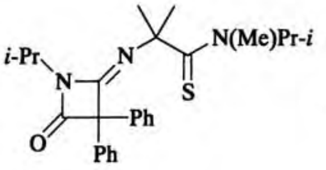
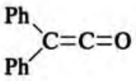
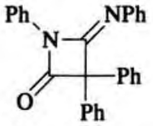
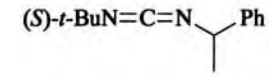
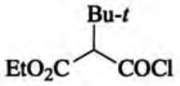
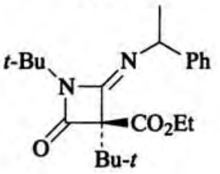
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PhCH_2COCl$	Et_3N, C_6H_{14}	 (—)	192
	 $Ph_2C=C=O$	Et_2O, 25°	 (90)	192
C_{12} 	 $Ph_2C=C=O$	25°	 (45)	193
C_{13} $PhN=C=NPh$	 $Ph_2C=C=O$	C_6H_6, 66°	 (60)	769
		Et_3N	 (28.5)	194

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

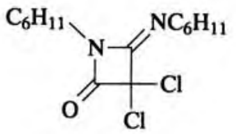
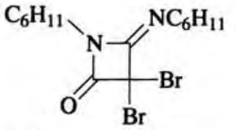
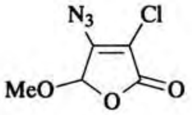
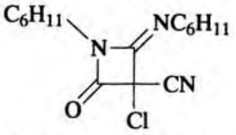
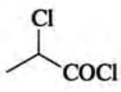
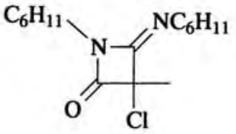
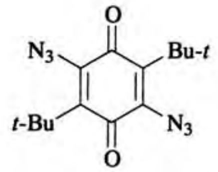
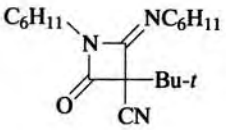
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6H_{11}N=C=NC_6H_{11}$	$Cl_2CHCOCl$	Et_3N, C_6H_6, rt	 (55)	769
	$Cl_2CHCOCl$	Et_3N, C_6H_{12}, 81°	" (72)	772
	$Br_2CHCOCl$	Et_3N, C_6H_{14}, 69°	 (59)	770
		C_6H_6, 80°	 (88)	311
		Et_3N, C_6H_{14}, 69°	 (25)	770
		C_6H_6	 (84)	353, 777

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

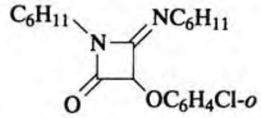
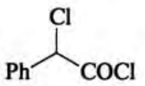
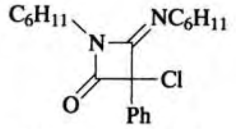
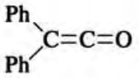
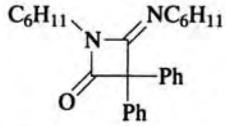
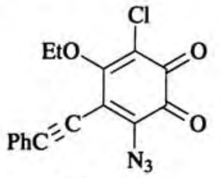
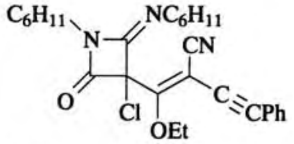
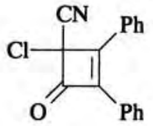
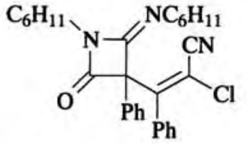
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	o-$ClC_6H_4OCH_2COCl$	Et_3N, C_6H_6, 25°	 (55)	769
		Et_3N, C_6H_{14}, 69°	 (65)	770
	 $Ph_2C=C=O$	C_6H_{14} or C_6H_6 rt	 (88-90)	769, 770
		C_6H_{12}, 80°	 (44)	778
		C_6H_6, 16 h	 (76)	114

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

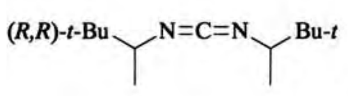
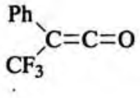
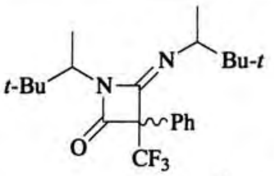
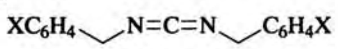
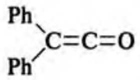
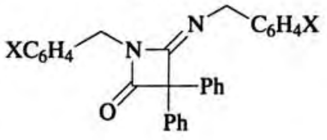
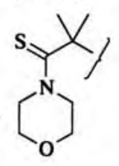
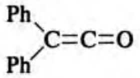
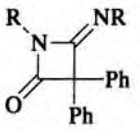
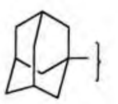
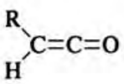
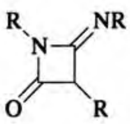
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph(CF_3)C=C=O$	—	 (84)	194
C_{15} 	 $Ph_2C=C=O$	C_6H_6, 25°		769
X: H			(49)	
X: p-Me			(48)	
X: p-MeO			(62)	
C_{17} RN=C=NR R = 	 $Ph_2C=C=O$	25°	 (26)	193
C_{21} RN=C=NR R = 	 $R(H)C=C=O$	—	 (20)	789

TABLE XXIII. [2+2] CYCLOADDITION OF KETENES TO CARBODIIMIDES (*Continued*)

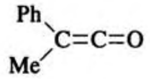
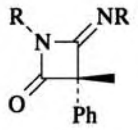
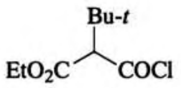
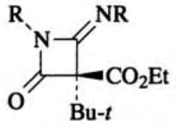
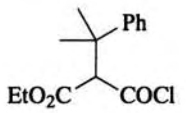
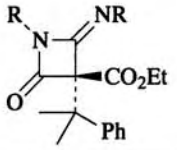
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RN=C=NR R = *l*-menthyl		—	 (37) $[\alpha]^{25}_{365}$ -439°	176
		Et_3N	 (64)	194
		Et_3N	 (75)	194

TABLE XXIV. [2+2] CYCLOADDITION OF KETENES TO *N*-SULFINYLAMINES

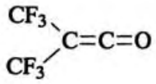
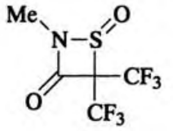
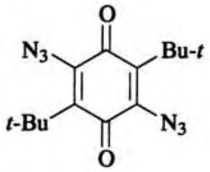
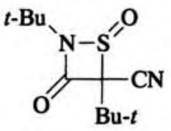
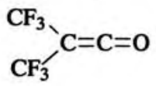
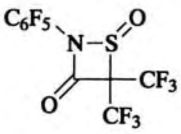
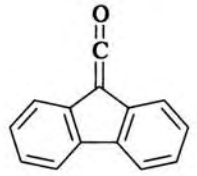
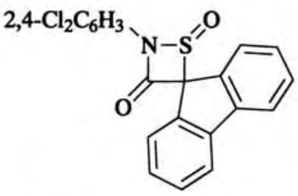
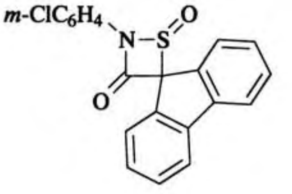
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_1					
MeN=S=O	 $(CF_3)_2C=C=O$	-30°		(83)	195
C_4					
t-BuN=S=O		C_6H_6, 80°		(88)	191
C_6					
$C_6F_5N=S=O$	 $(CF_3)_2C=C=O$	-30°		(57)	195
2,4-$Cl_2C_6H_3N=S=O$		Pet. ether		(83)	196
m-$ClC_6H_4N=S=O$	"	60°, 72 h		(87)	196

TABLE XXIV. [2+2] CYCLOADDITION OF KETENES TO *N*-SULFINYLAMINES (*Continued*)

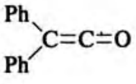
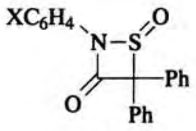
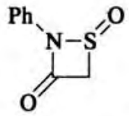
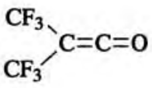
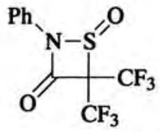
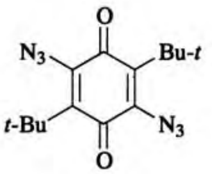
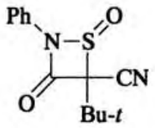
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$XC_6H_4N{=}S{=}O$		20°, 50 min; 60°, 72 h		196
X				
2,4-Cl_2			(83)	
o-Cl			(93)	
m-Cl			(89)	
p-Cl			(99)	
p-O_2N			(86)	
H			(95)	
$PhN{=}S{=}O$	$CH_2{=}C{=}O$	Me_2CO, -78°	 (100)	202, 197
		-30°	 (—)	195
		C_6H_6, 80°	 (—)	191

TABLE XXIV. [2+2] CYCLOADDITION OF KETENES TO *N*-SULFINYLAMINES (*Continued*)

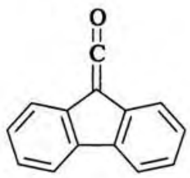
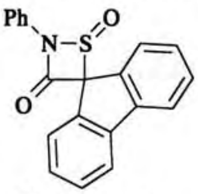
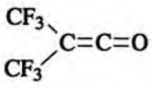
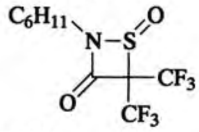
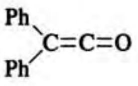
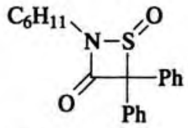
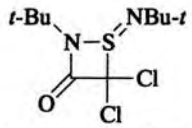
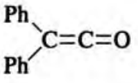
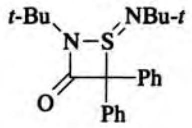
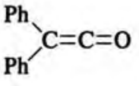
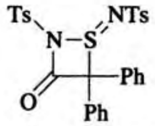
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Pet. ether	 (96)	196
		-30°	 (86)	195
		rt	 (99)	196
C_8 *t*-BuN=S=NBu-*t*	$Cl_2CHCOCl$	Et_3N	 (91)	198
		Et_2O, 0°	 (74)	780
C_{14} TsN=S=NTs		$CHCl_3$, -15°	 (100)	781

TABLE XXV. [2+2] CYCLOADDITION OF KETENES TO NITROSO COMPOUNDS

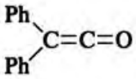
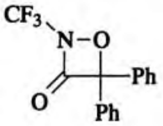
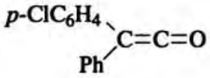
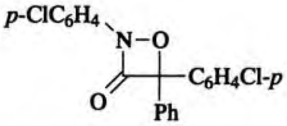
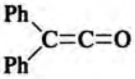
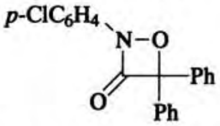
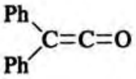
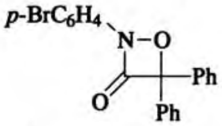
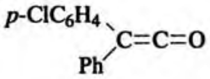
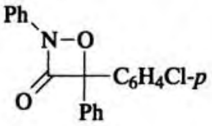
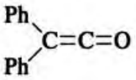
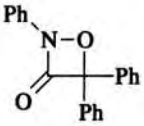
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_1 CF_3NO	 $Ph_2C{=}C{=}O$	—	 (—)	782
p-ClC_6H_4NO	 $(p\text{-}ClC_6H_4)(Ph)C{=}C{=}O$	Pet. ether	 (38)	200
	 $Ph_2C{=}C{=}O$	Pet. ether	 (48)	200
p-BrC_6H_4NO	 $Ph_2C{=}C{=}O$	Pet. ether	 (19)	200
PhNO	 $(p\text{-}ClC_6H_4)(Ph)C{=}C{=}O$	Pet. ether	 (52)	200
	 $Ph_2C{=}C{=}O$	Pet. ether	 **I** (45-63)	200, 783

TABLE XXV. [2+2] CYCLOADDITION OF KETENES TO NITROSO COMPOUNDS (*Continued*)

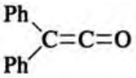
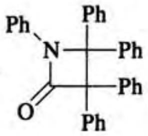
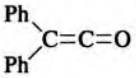
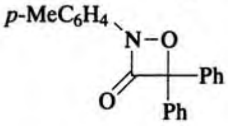
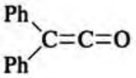
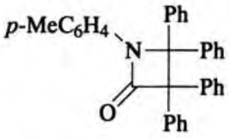
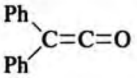
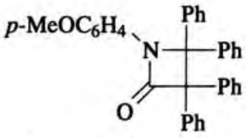
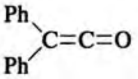
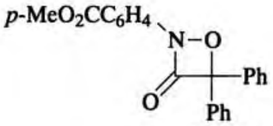
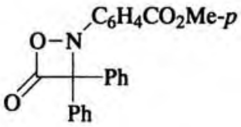
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C{=}C{=}O$	$CHCl_3$, 25°	**I** (60) +  (13)	199
C_7 p-MeC_6H_4NO	 $Ph_2C{=}C{=}O$	Pet. ether	 (38)	200
	 $Ph_2C{=}C{=}O$	$CHCl_3$, 25°	 (13)	199
p-$MeOC_6H_4NO$	 $Ph_2C{=}C{=}O$	$CHCl_3$, 25°	 (22)	199
C_8 p-$MeO_2CC_6H_4NO$	 $Ph_2C{=}C{=}O$	$CHCl_3$, 25°	 (72) +  (28)	199

TABLE XXV. [2+2] CYCLOADDITION OF KETENES TO NITROSO COMPOUNDS (*Continued*)

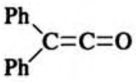
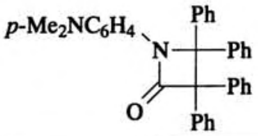
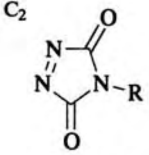
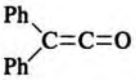
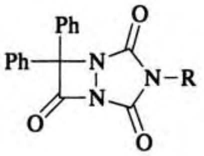
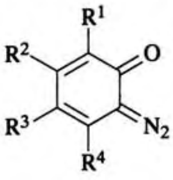
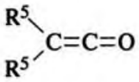
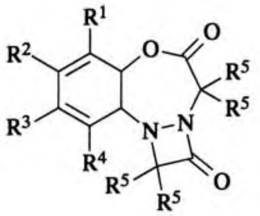
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	$CHCl_3$, 25°	 (61-65)	199, 783

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2  R = Me, Et, *n*-Pr, *n*-Bu, Ph		CH_2Cl_2, 0°	 (49-54)	783a
				

R^1	R^2	R^3	R^4	R^5	Conditions	Yield (%)	Refs.
Cl	Cl	Cl	Cl	Ph	Xylene, rt	(45)	206
H	Cl	H	Cl	Ph	Xylene, rt	(81)	206
H	Cl	H	H	Me	Et_2O, 35°, 3 h	(60)	668
H	H	Cl	H	Me	Et_2O, 35°, 3 h	(58)	668
H	Br	H	H	Me	Et_2O, 35°, 3 h	(40)	668
H	H	Br	H	Me	Et_2O, 35°, 3 h	(40)	668
H	NO_2	H	H	Ph	Xylene, rt	(51)	206
Me	Cl	Me	H	Ph	Xylene, rt	(47)	206
H	*t*-Bu	H	*t*-Bu	Ph	Xylene, rt	(85)	206
H	*t*-Bu	H	*t*-Bu	Me	Et_2O, 35°, 3 h	(52)	668

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

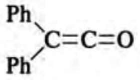
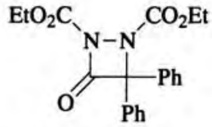
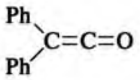
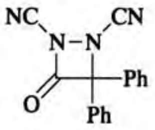
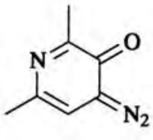
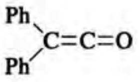
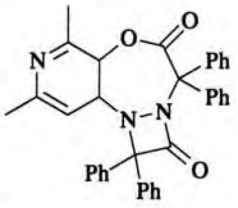
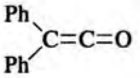
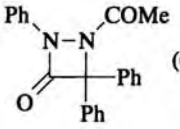
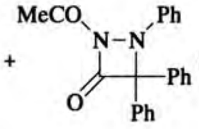
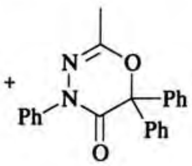
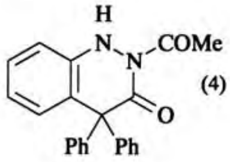
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$EtO_2CN{=}NCO_2Et$		Pet. ether, 24 h	 (70)	204
C_7				
NCN=NCN		—	 (—)	784
		Xylene, rt	 (38)	206
C_8				
PhN=NCOMe		C_6H_6, rt	 (60) +  (26) +  (10) +  (4)	205

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

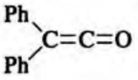
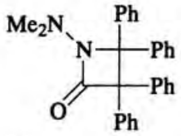
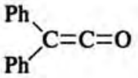
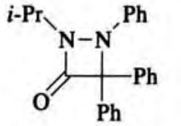
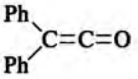
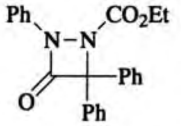
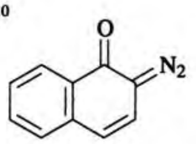
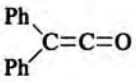
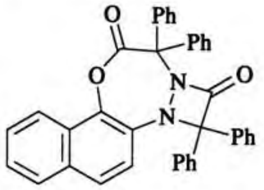
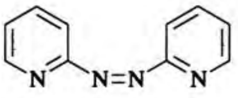
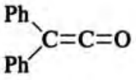
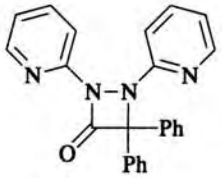
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$PhN{=}NNMe_2$		hν	 (35)	785
C_9				
PhN=NPr-*i*		hν	 (11)	785, 78
$PhN{=}NCO_2Et$		hν, C_6H_{12}	 (69)	785, 78
C_{10}				
		Xylene, rt	 (75)	206
		C_6H_6	 (55)	787

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

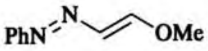
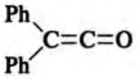
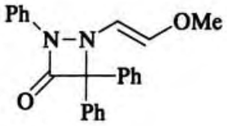
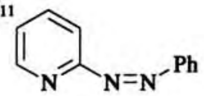
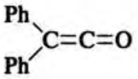
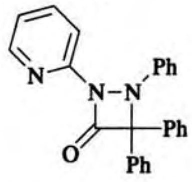
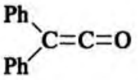
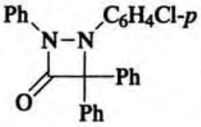
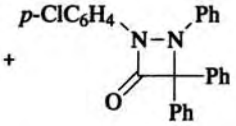
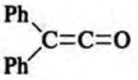
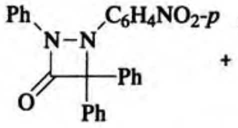
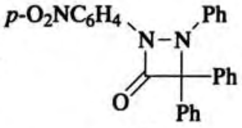
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6	 (85)	268
C_{11}				
		—	 (71)	787
C_{12}				
$PhN=NC_6H_4Cl$-*p*		*hν*, C_6H_6	 +  I II (78) I:II = 59:41	786
$PhN=NC_6H_4NO_2$-*p*		*hν*, C_6H_6	 +  I II (94) I:II = 61:39	786

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

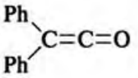
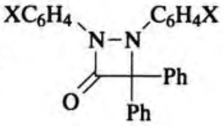
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$XC_6H_4N=NC_6H_4X$		*hν*, C_6H_6 or Et_2O		
X				
o-Cl			(91)	201
m-Cl			(55)	201
p-Cl			(17)	201
m-Br			(76)	201
p-Br			(14)	201
o-NO_2			(20)	201
m-NO_2			(37)	201
p-Me			(78)	788
m-Me			(15)	788
o-Me			(73)	788
o-OMe			(19)	201
m-OMe			(69)	201
p-OMe			(71)	201
p-CO_2Et			(33)	201

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

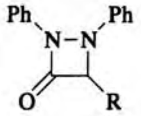
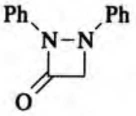
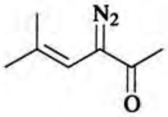
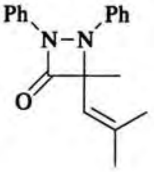
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
PhN=NPh	$RCOCHN_2$	hν, solvent		
	R	Solvent		
	Ph	C_6H_6	(31)	314, 789
	1-$C_{10}H_7$	CH_2Cl_2	(30)	789
	p-$MeOC_6H_4$	CH_2Cl_2	(53)	789
	m-$MeOC_6H_4$	CH_2Cl_2	(57)	789
	p-MeC_6H_4	CH_2Cl_2	(42)	789
	p-BrC_6H_4	CH_2Cl_2	(48)	789
	o-BrC_6H_4	CH_2Cl_2	(20)	789
	p-ClC_6H_4	CH_2Cl_2	(42)	789
	m-ClC_6H_4	CH_2Cl_2	(13)	789
	o-ClC_6H_4	CH_2Cl_2	(9)	789
	p-$O_2NC_6H_4$	CH_2Cl_2	(47)	789
	m-$O_2NC_6H_4$	CH_2Cl_2	(43)	789
	o-$O_2NC_6H_4$	CH_2Cl_2	(5)	789
cis-PhN=NPh	$CH_2{=}C{=}O$	MeOH	 (68)	790
trans-PhN=NPh	$CH_2{=}C{=}O$	hν, C_6H_{14}, 15°	" (—)	791
		hν	 (—)	288

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

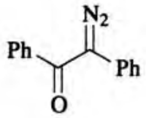
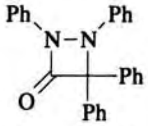
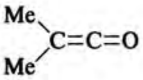
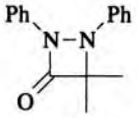
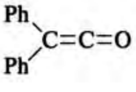
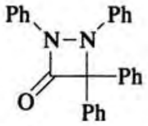
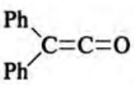
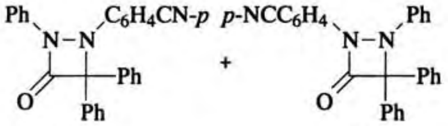
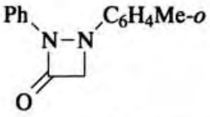
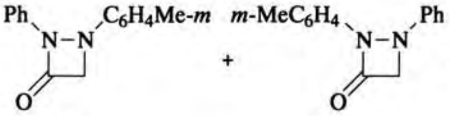
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		hν, C_6H_6	 (32)	314, 79
cis-PhN=NPh	 $Me_2C{=}C{=}O$	Et_2O or MeOH	 (40)	790
trans-PhN=NPh	 $Ph_2C{=}C{=}O$	hν, Et_2O	 (71)	201, 786 788
C_{13}				
PhN=NC_6H_4CN-*p*	 $Ph_2C{=}C{=}O$	hν, C_6H_6	 **I** **II** (—) **I**:**II** = 64:36	786
PhN=NC_6H_4Me-*o*	$CH_2{=}C{=}O$	hν	 (81)	203
PhN=NC_6H_4Me-*m*	$CH_2{=}C{=}O$	hν	 (29) (36)	203

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

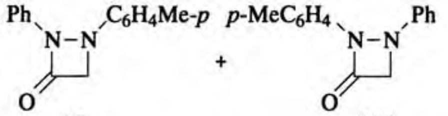
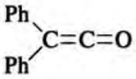
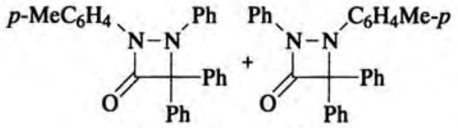
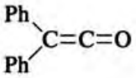
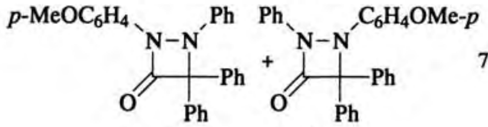
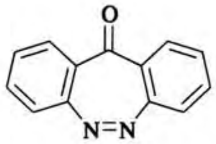
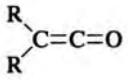
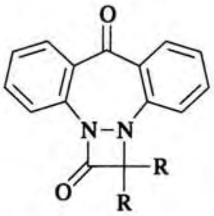
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$PhN{=}NC_6H_4Me\text{-}p$	$CH_2{=}C{=}O$	hν	 (7) + (50)	203
	 $Ph_2C{=}C{=}O$	hν, C_6H_6	 (38) + (45)	786
$PhN{=}NC_6H_4OMe\text{-}p$	 $Ph_2C{=}C{=}O$	hν, C_6H_6	 (25) + (45)	785, 786
	 $R_2C{=}C{=}O$	PhMe, 30-35°		202
	R			
	H		(10)	
	Me		(30)	
	Ph		(80)	

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

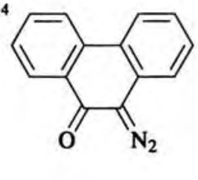
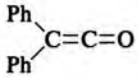
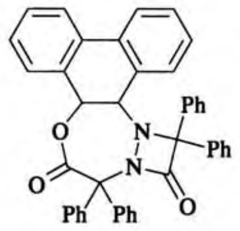
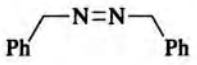
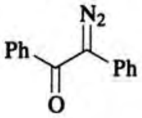
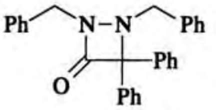
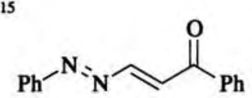
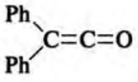
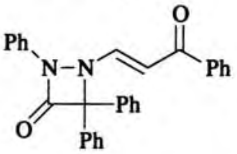
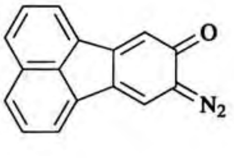
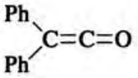
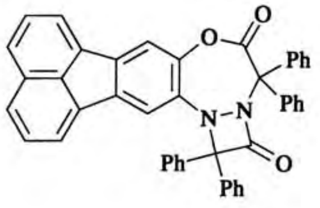
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
	 $Ph_2C{=}C{=}O$	Xylene, rt	 (70)	206
		hν, C_6H_6	 (50)	788
C_{15}				
	 $Ph_2C{=}C{=}O$	C_6H_6	 (86)	268
	 $Ph_2C{=}C{=}O$	Xylene, rt	 (31)	206

TABLE XXVI. [2+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

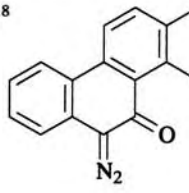
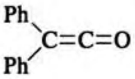
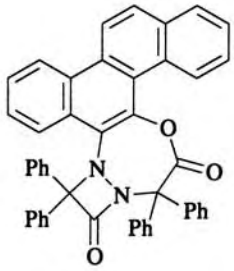
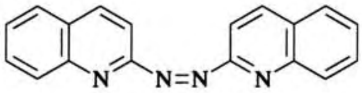
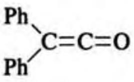
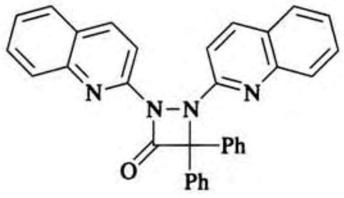
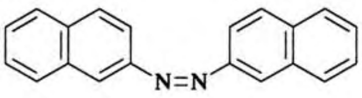
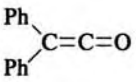
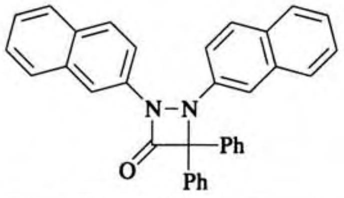
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$Ph_2C=C=O$	Xylene, rt	 (56)	206
	$Ph_2C=C=O$	Dioxane, 3 h	 (31)	787
C_{20} 	$Ph_2C=C=O$	*h*ν, pet. ether	 (9)	788

TABLE XXVII. [3+2] CYCLOADDITIONS

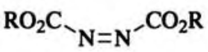
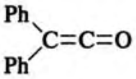
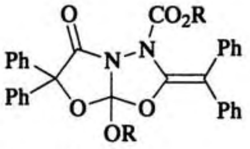
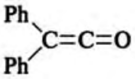
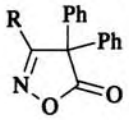
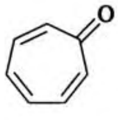
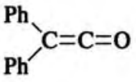
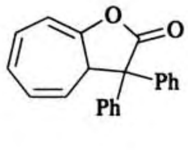
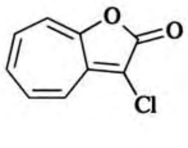
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
 $RO_2C-N=N-CO_2R$	 $Ph_2C=C=O$	C_6H_6	 R = Et (—) R = Ph (80) R = Bn (80)	793
C_7				
$RC\equiv\overset{+}{N}-\overset{-}{O}$	 $Ph_2C=C=O$	PhMe		210, 211
R				
p-ClC_6H_4			(60)	
p-BrC_6H_4			(60)	
p-$Me_2NC_6H_4$			(75)	
o-ClC_6H_4			(65)	
m-$O_2NC_6H_4$			(70)	
t-Bu			(—)	
PhCH=CH			(80)	
	 $Ph_2C=C=O$	C_6H_6, 78°, 1 h	 (99)	539
	$Cl_2CHCOCl$	Et_3N, Et_2O, 0°	 (19)	316

TABLE XXVII. [3+2] CYCLOADDITIONS (*Continued*)

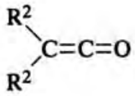
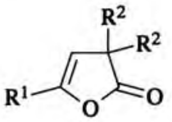
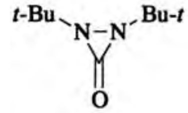
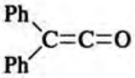
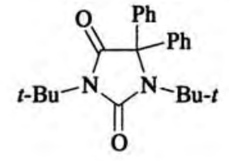
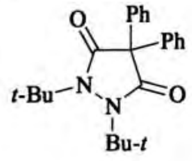
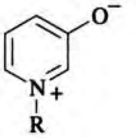
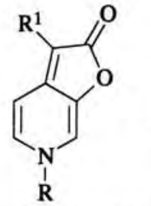
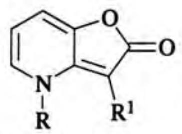
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 R^1COCHN_2	 $R^2_2C{=}C{=}O$	Et_2O, 35°, 70 h	 R^1 / R^2 / Yield n-$C_{11}H_{23}$ / Me / (69) n-$C_{15}H_{31}$ / Me / (55) Bn / Me / (21) p-$MeOC_6H_4$ / Me / (38) Ph / H / (—) p-$MeOC_6H_4$ / Ph / (—) p-$O_2NC_6H_4$ / Ph / (—)	222
	 $Ph_2C{=}C{=}O$	PhMe, 110°, 10 h	 +  (32) (26)	794
	Various haloketenes	—	 +  R, R^1 = various aryl and alkyl groups	230

TABLE XXVII. [3+2] CYCLOADDITIONS (*Continued*)

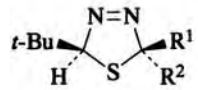
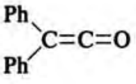
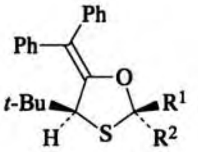
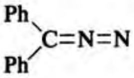
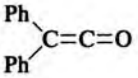
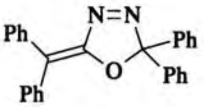
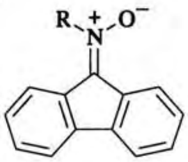
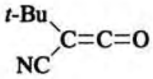
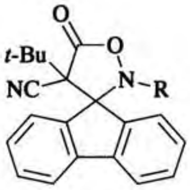
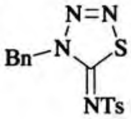
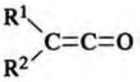
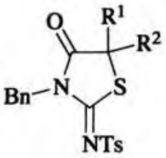
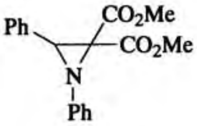
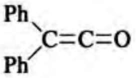
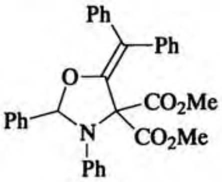
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	 $Ph_2C{=}C{=}O$	100°, 5 h	 (85-94) R^1 = t-Bu, R^2 = H R^1 = H, R^2 = t-Bu	326
C_{12}  $Ph_2C{=}N{=}N$	 $Ph_2C{=}C{=}O$	C_6H_6, 78° 12 h	 (—)	795, 79
C_{13} 	 $(t\text{-}Bu)(NC)C{=}C{=}O$	110°, 12 h	 R = Me (72) R = Et (65)	209
C_{14} 	 $R^1R^2C{=}C{=}O$	CCl_4	 R^1 = R^2 = Ph (54) R^1 = CN, R^2 = t-Bu (40)	797
C_{18} 	 $Ph_2C{=}C{=}O$	PhMe, 110°	 (—)	208

TABLE XXVII. [3+2] CYCLOADDITIONS (*Continued*)

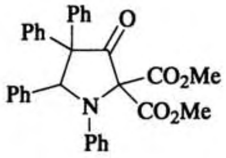
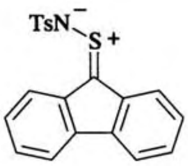
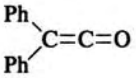
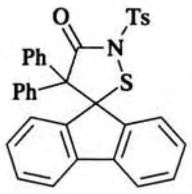
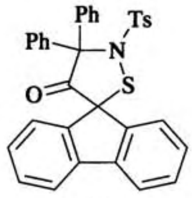
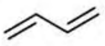
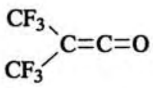
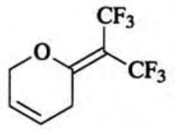
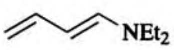
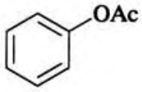
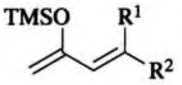
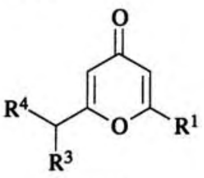
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2=C=O$	PhMe, 110°	 (—)	208
C_{19} 	 $Ph_2C=C=O$	$Cl(CH_2)_2Cl$ rt, 1 week	 (27) +  (9)	766

TABLE XXVIII. [4+2] CYCLOADDITION OF KETENES TO DIENES

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4				
	 $(CF_3)_2C{=}C{=}O$	70°, 35 h	 (90)	231, 323
	$CH_2{=}C{=}O$	Et_2O, 0°	 (4)	240
	$R^3R^4CHCOCl$	Et_3N, Et_2O; MeOH, H^+		238

R^1	R^2	R^3	R^4	
H	OMe	Cl	Cl	(56)
H	OMe	H	Cl	(55)
H	OTMS	Ph	Ph	(55)
Me	OTMS	H	Cl	(55)
Me	OTMS	Cl	Cl	(52)
Me	OTMS	Ph	Ph	(70)

TABLE XXVIII. [4+2] CYCLOADDITION OF KETENES TO DIENES (*Continued*)

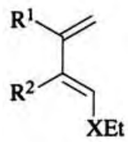
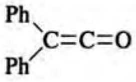
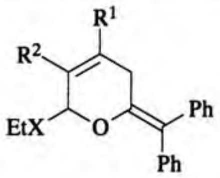
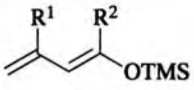
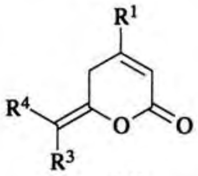
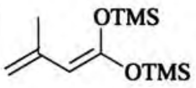
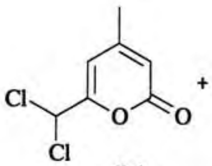
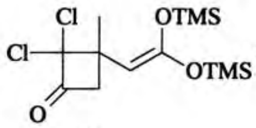
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	CCl_4		237
X R^1 R^2				
O Me H			(—)	
S Me H			(—)	
O H Me			(—)	
O Me Me			(—)	
O *i*-Pr H			(—)	
	$R^3R^4CHCOCl$	Et_3N, Et_2O, 0°		235
R^1 R^2	R^3 R^4			
OMe OMe	H Cl		(23)	
OMe OMe	Cl Cl		(30)	
OMe OMe	Ph Ph		(56)	
Me OTMS	Ph Ph		(68)	
C_5				
	$Cl_2CHCOCl$	Et_3N, Et_2O, 0°	 +  (31) (55)	235

TABLE XXVIII. [4+2] CYCLOADDITION OF KETENES TO DIENES (*Continued*)

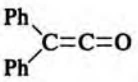
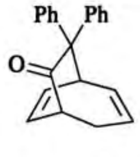
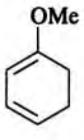
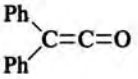
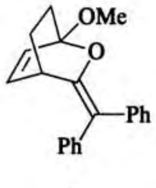
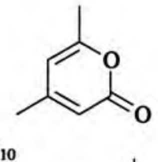
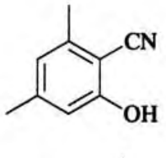
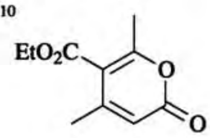
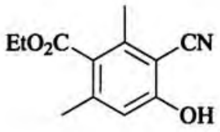
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
	 $Ph_2C=C=O$	C_6H_6, 80°, 144 h	 (11)	233
	 $Ph_2C=C=O$	CCl_4	 (—)	237
	$NCCH_2CO_2Et$	200°, 70 h	 (10)	239
C_{10}				
	$NCCH_2CO_2Et$	195-200°, 122 h	 (13)	239

TABLE XXVIII. [4+2] CYCLOADDITION OF KETENES TO DIENES (*Continued*)

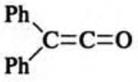
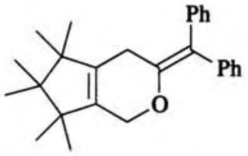
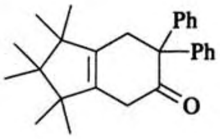
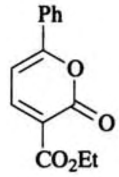
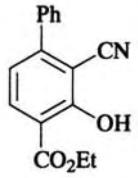
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_{12}, 55°, 15 d	 (35) +  (35)	234
	$NCCH_2CO_2Et$	195-200°, 75 h	 (56)	239

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES

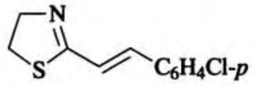
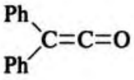
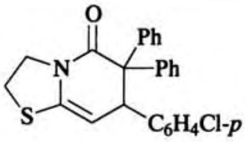
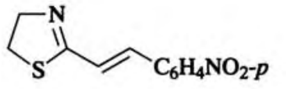
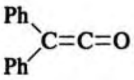
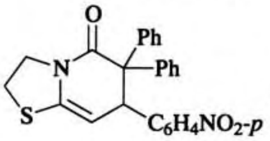
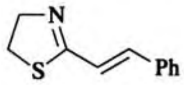
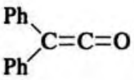
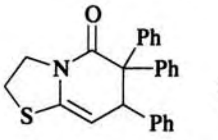
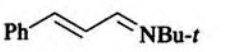
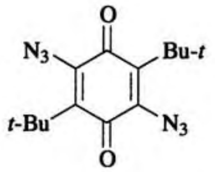
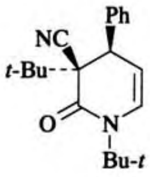
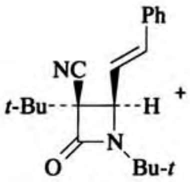
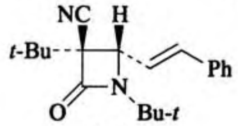
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}				
	 $Ph_2C=C=O$	Xylene, 137°, 10 h	 (48)	243
	 $Ph_2C=C=O$	Xylene, 137°, 10 h	 (78)	243
	 $Ph_2C=C=O$	Xylene, 137°, 10 h	 (78)	243
C_{13}				
		C_6H_6, 80°	 (52) +  (17) +  (—)	23

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

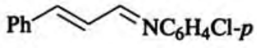
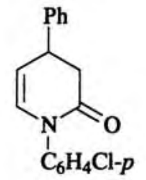
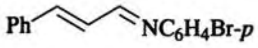
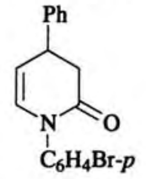
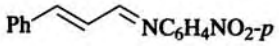
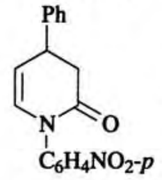
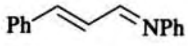
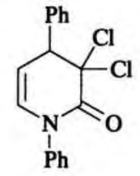
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{15}					
	$BrCH_2CO_2Et$	Zn, C_6H_6		(70)	241
	$BrCH_2CO_2Et$	Zn, C_6H_6		(90)	241
	$BrCH_2CO_2Et$	Zn, C_6H_6		(16)	241
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 20°		(45)	242

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

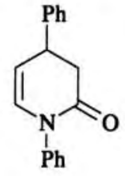
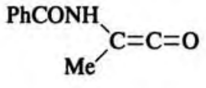
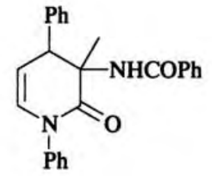
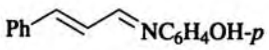
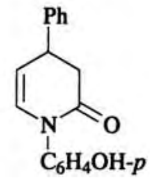
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$BrCH_2CO_2Et$	Zn, C_6H_6		(62)	241
	 $PhCONH(Me)C{=}C{=}O$	—		(—)	798
	$BrCH_2CO_2Et$	Zn, C_6H_6		(65)	241

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

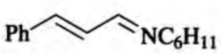
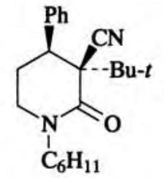
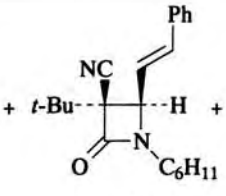
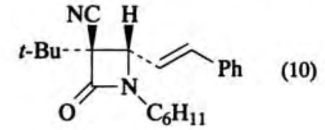
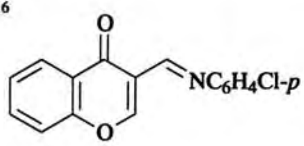
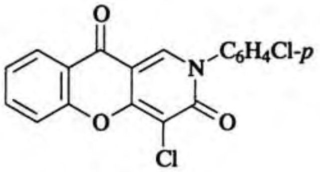
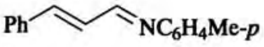
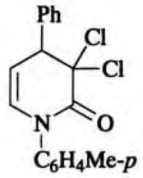
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15} 		C_6H_6, 80°	 (23) +  (64) +  (10)	23
C_{16} 	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°	 (54)	244
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 20°	 (67)	242

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

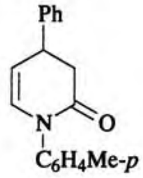
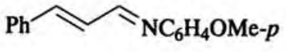
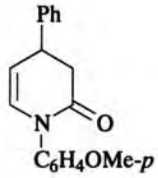
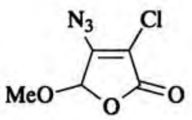
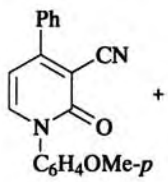
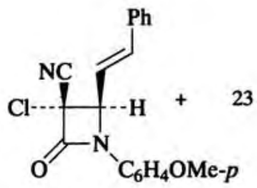
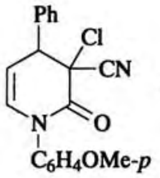
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$BrCH_2CO_2Et$	Zn, C_6H_6	 (34)	241
	$BrCH_2CO_2Et$	Zn, C_6H_6	 (68)	241
		C_6H_6, 80°	 (22) +  (17) +  (42)	23

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

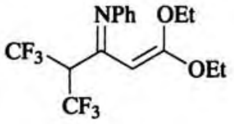
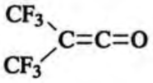
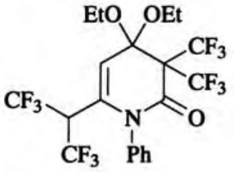
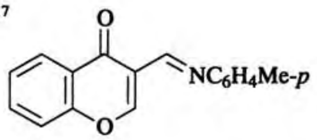
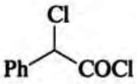
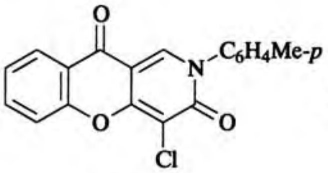
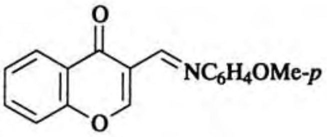
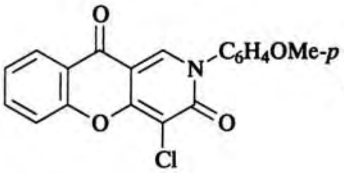
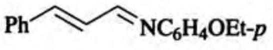
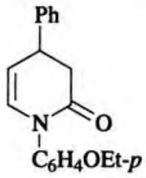
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $(CF_3)_2C=C=O$	—	 (73)	799
C_{17} 	 $PhCHClCOCl$	Et_3N, C_6H_6, 80°	 (21)	244
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°	 (74)	244
	$BrCH_2CO_2Et$	Zn, C_6H_6	 (74)	241

TABLE XXIX. [4+2] CYCLOADDITION OF KETENES TO AZADIENES (*Continued*)

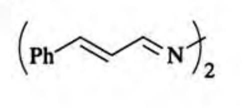
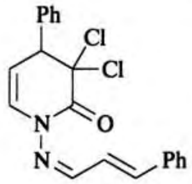
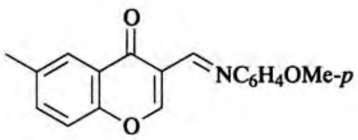
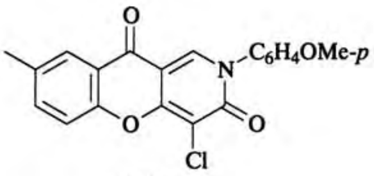
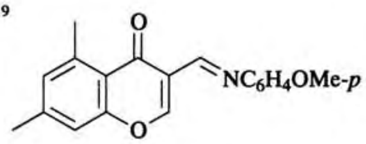
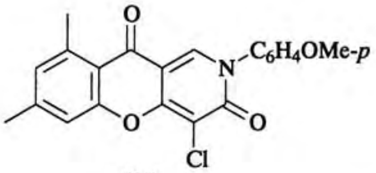
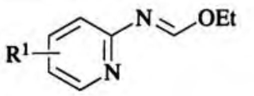
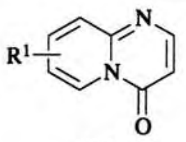
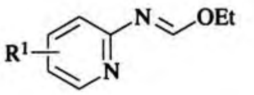
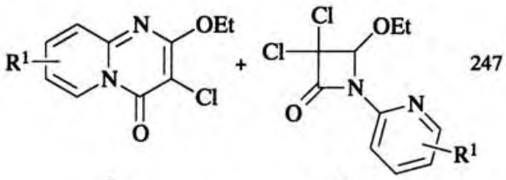
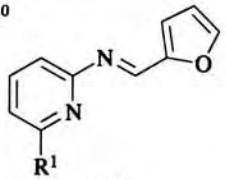
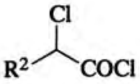
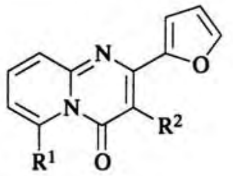
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$Cl_2CHCOCl$	Et_3N, C_6H_6, 20°	 (75)	242
	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°	 (72)	244
C_{19} 	$Cl_2CHCOCl$	Et_3N, C_6H_6, 80°	 (85)	244

TABLE XXX. [4+2] CYCLOADDITION OF KETENES TO AMIDINES

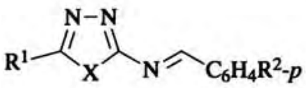
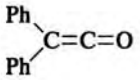
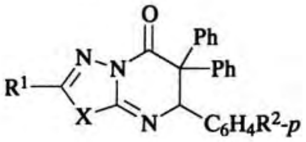
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
	$CH_2=C=O$	75°		800
R^1				
H			(58)	
6-Me			(25)	
5-Me			(68)	
4-Me			(44)	
3-Me			(85)	
	$Cl_2CHCOCl$	Et_3N, Et_2O	 I II	247

R^1	I	II
H	(45)	(7)
6-Me	(43)	(—)
5-Me	(36)	(7)
4-Me	(21)	(—)
3-Me	(80)	(—)

TABLE XXX. [4+2] CYCLOADDITION OF KETENES TO AMIDINES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}				
		Et_3N, Et_2O		246

R^1	R^2	Product(s) and Yield(s) (%)
H	Cl	(78)
H	Ph	(40)
Me	Cl	(43)
Me	H	(20)
Me	Ph	(35)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		Xylene, 137°		

X	R^1	R^2	Product(s) and Yield(s) (%)	Refs.
S	H	OMe	(87)	248, 801
S	Me	NO_2	(79)	248
S	Me	OMe	(67)	248
S	Me	NMe_2	(63)	248
O	Ph	NO_2	(36)	248
Se	Ph	NO_2	(78)	248
O	Ph	OMe	(58)	248
Se	Ph	OMe	(54)	248
O	Ph	NMe_2	(33)	248
Se	Ph	NMe_2	(43)	248

TABLE XXX. [4+2] CYCLOADDITION OF KETENES TO AMIDINES (*Continued*)

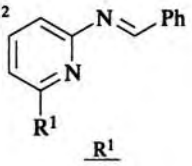
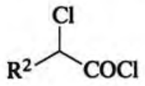
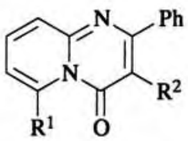
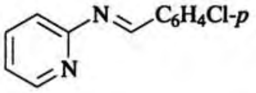
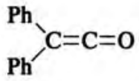
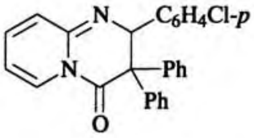
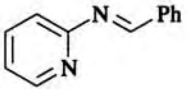
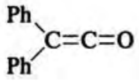
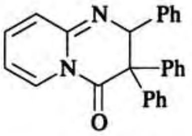
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12} 		Et_3N, Et_2O		246
R^1	R^2			
H	Cl		(35)	
H	Ph		(37)	
Me	H		(34)	
Me	Cl		(70)	
Me	Ph		(32)	
	 $Ph_2C=C=O$	C_6H_6, 25°	 (86)	802
	 $Ph_2C=C=O$	C_6H_6, 25°	 (87)	802

TABLE XXX. [4+2] CYCLOADDITION OF KETENES TO AMIDINES (*Continued*)

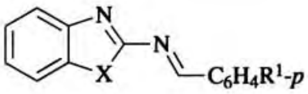
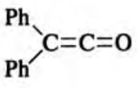
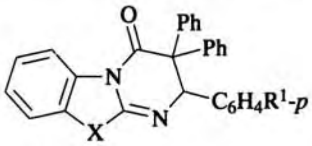
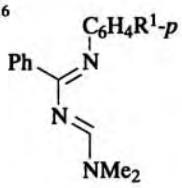
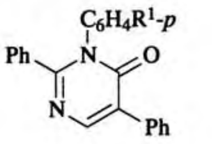
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	 $Ph_2C=C=O$	Xylene, 137°		
X R^1			X	
O NO_2			O (86)	248
S NO_2			S (70)	248
NH NO_2			$NCOCHPh_2$ (75)	248
O OMe			O (74)	248, 801
S OMe			S (87)	248, 801
NH OMe			$NCOCHPh_2$ (81)	248, 801
O NMe_2			O (50)	248
S NMe_2			S (91)	248
NH NMe_2			$NCOCHPh_2$ (84)	248
C_{16} 	$PhCH_2COCl$	Et_3N, C_6H_6		803
R^1				
Cl			(86)	
Br			(84)	
H			(86)	
Me			(92)	

TABLE XXX. [4+2] CYCLOADDITION OF KETENES TO AMIDINES (*Continued*)

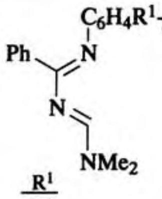
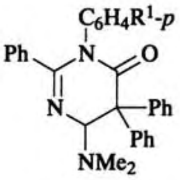
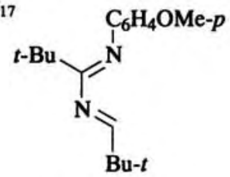
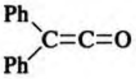
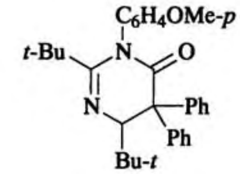
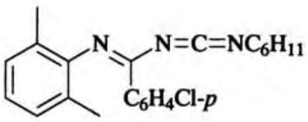
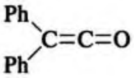
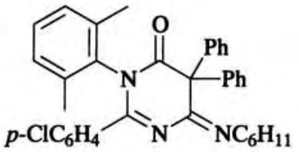
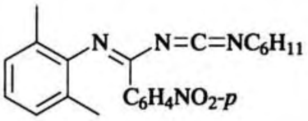
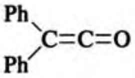
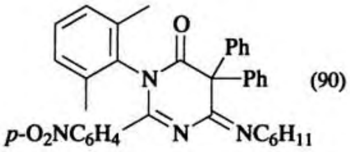
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Ph_2CHCOCl$	Et_3N, C_6H_6		803
R^1				
Cl			(85)	
Br			(96)	
H			(91)	
Me			(95)	
C_{17} 	 $Ph_2C=C=O$	—	 (52)	245
	 $Ph_2C=C=O$	CH_2Cl_2	 (33)	249
	 $Ph_2C=C=O$	CH_2Cl_2	 (90)	249

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES

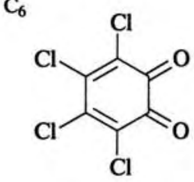
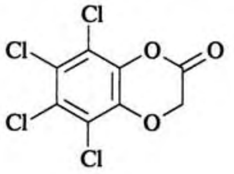
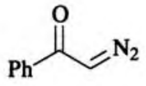
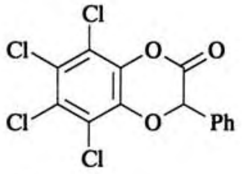
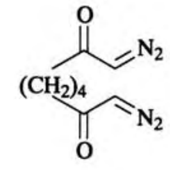
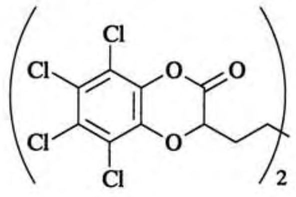
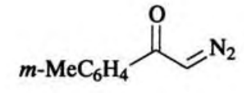
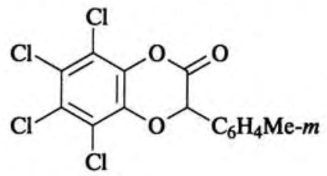
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	$CH_2{=}C{=}O$	-70°, 2 d	 (8)	804
		PhMe, 111°	 (27)	804, 805
		PhMe, 111°	 (78)	250
		PhMe, 111°	 (62)	250

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

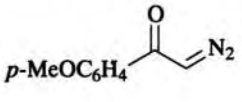
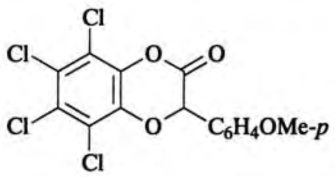
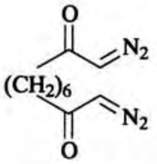
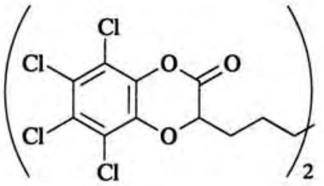
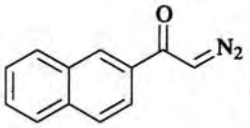
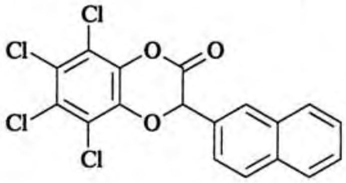
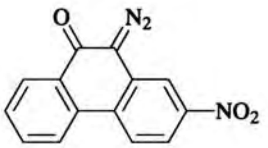
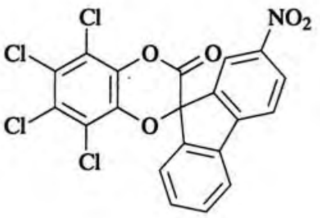
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 111°	 (64)	250
		PhMe, 111°	 (32)	250
		PhMe, 111°	 (59)	250
		—	 (—)	805

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

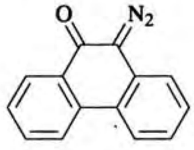
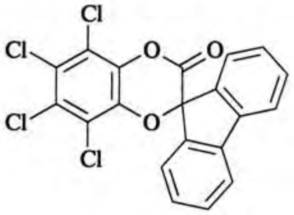
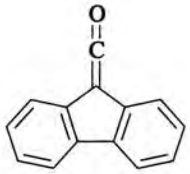
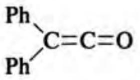
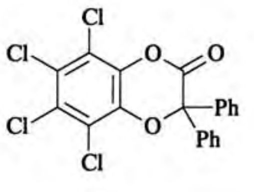
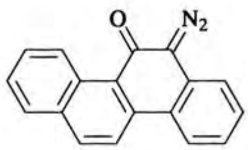
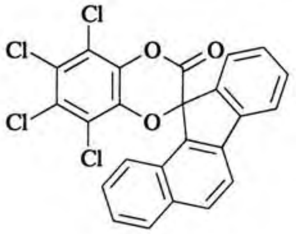
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 111°	 (30)	804, 80
		Et_2O	" (39)	804
	 $Ph_2C=C=O$	Et_2O	 (80)	314
		PhMe, 111°	 (40)	804, 805

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

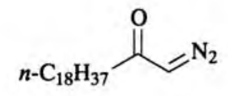
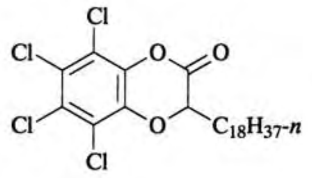
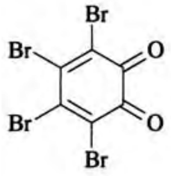
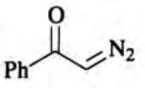
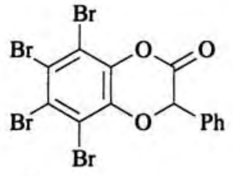
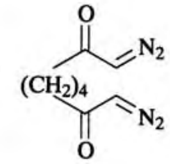
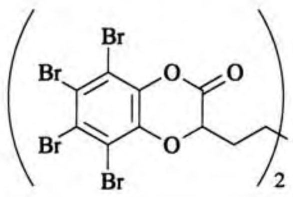
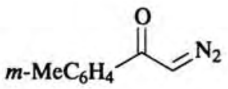
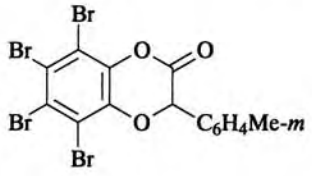
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 111°	 (77)	250
		PhMe, 111°	 (58)	250
		PhMe, 111°	 (71)	250
		PhMe, 111°	 (45)	250

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

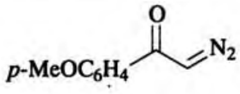
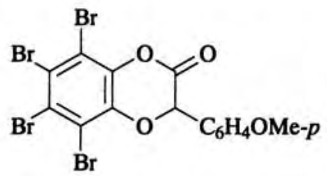
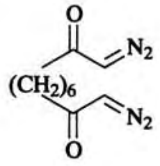
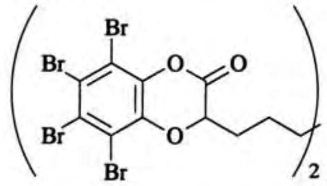
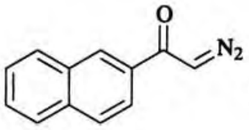
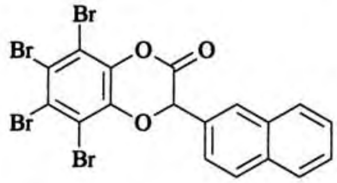
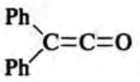
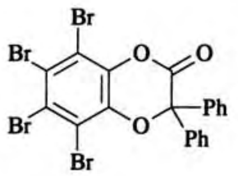
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 111°	 (73)	250
		PhMe, 111°	 (15)	250
		PhMe, 111°	 (38)	250
	 $Ph_2C=C=O$	Et_2O	 (48)	314

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

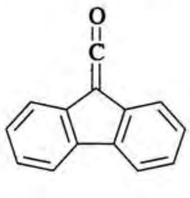
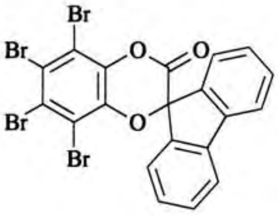
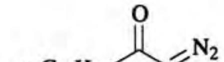
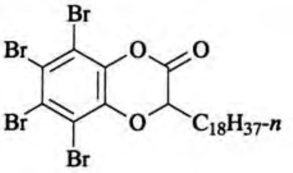
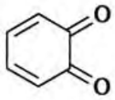
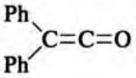
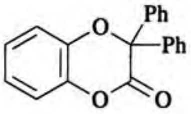
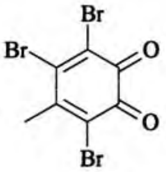
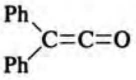
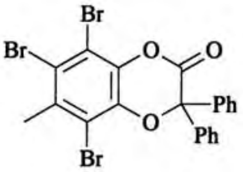
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
		Et_2O		(34)	804
		PhMe, 111°		(50)	250
	 $Ph_2C=C=O$	C_6H_6		(82)	806
C_7 	 $Ph_2C=C=O$	PhMe, 10 min		(65)	804

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

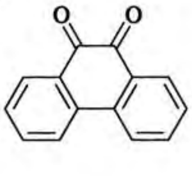
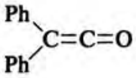
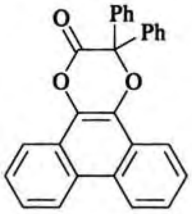
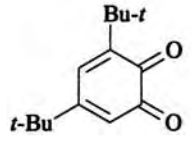
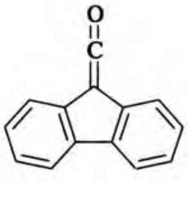
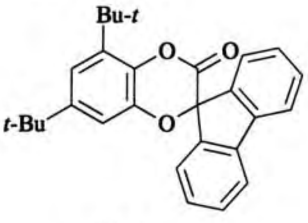
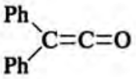
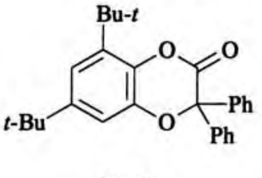
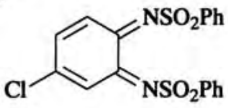
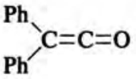
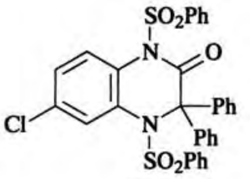
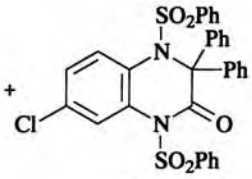
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{14} 	 $Ph_2C=C=O$	*h*ν, C_6H_6, 36 d		(—)	154, 80
		Et_2O		(43)	804
	 $Ph_2C=C=O$	PhMe		(96)	804
C_{18} 	 $Ph_2C=C=O$	C_6H_6	 (32) +  (32)		251

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

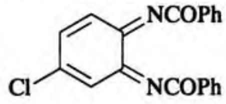
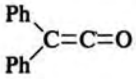
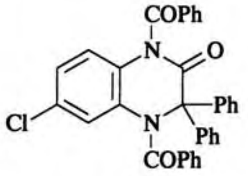
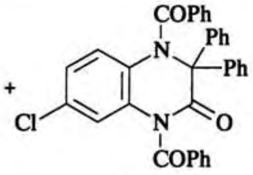
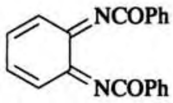
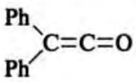
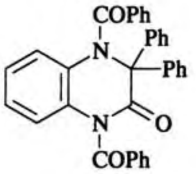
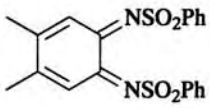
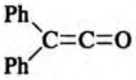
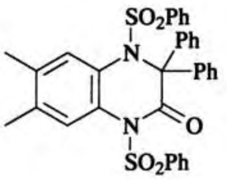
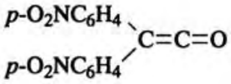
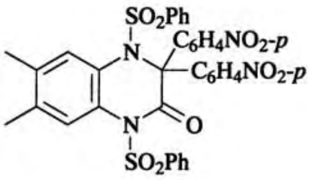
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{20} 	 $Ph_2C=C=O$	C_6H_6	 (37) +  (44)	251
	 $Ph_2C=C=O$	C_6H_6	 (76)	251
	 $Ph_2C=C=O$	C_6H_6	 (90)	251
	 $(p\text{-}O_2NC_6H_4)_2C=C=O$	C_6H_6	 (76)	251

TABLE XXXI. [4+2] CYCLOADDITION OF KETENES TO *O*-QUINONES AND QUINONIMINES (*Continued*)

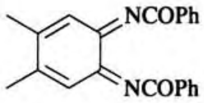
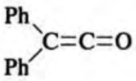
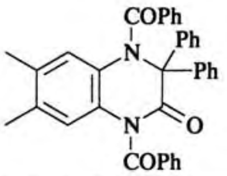
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	 $Ph_2C=C=O$	C_6H_6	 (8)	251

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS

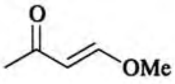
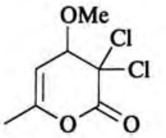
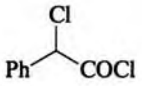
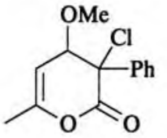
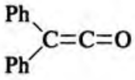
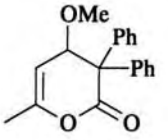
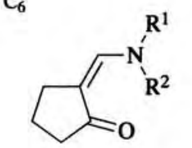
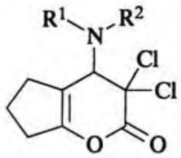
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}		(—)	327
		Et_3N, C_6H_{14}		(—)	327
	 $Ph_2C=C=O$	82°		(78)	327
C_6 	$Cl_2CHCOCl$	Et_3N, C_6H_6			808
R^1 R^2 *i*-Pr *i*-Pr Me Ph Ph Ph			(54) (48) (42)		

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

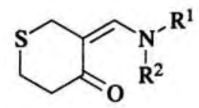
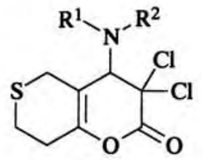
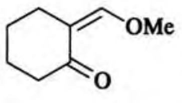
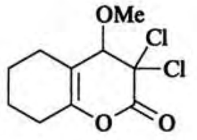
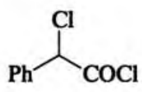
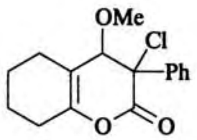
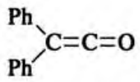
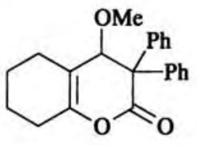
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Cl_2CHCOCl$	Et_3N, Et_2O			258
R^1 R^2 *i*-Pr *i*-Pr Me Ph Ph Ph			(40) (36) (42)		
C_7 	$Cl_2CHCOCl$	Et_3N, C_6H_{14}		(—)	327
		Et_3N, C_6H_{14}		(68)	327
	 $Ph_2C=C=O$	82°		(90)	327

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

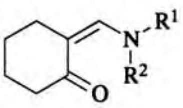
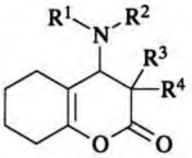
Reactant		Ketene or Ketene Source		Conditions	Product(s) and Yield(s) (%)	Refs.
		$R^3R^4CHCOCl$		Et_3N, C_6H_6		
R^1	R^2	R^3	R^4			
Me	Me	SEt	SEt		(81)	809
Et	Et	$S(CH_2)_3S$			(63)	810
i-Pr	*i*-Pr	Cl	Cl		(61)	808
Morpholino		$S(CH_2)_3S$			(30)	810
Morpholino		SEt	SEt		(40)	809
Piperidino		$S(CH_2)_3S$			(45)	810
Piperidino		SEt	SEt		(38)	809
Me	Ph	Cl	Cl		(51)	808
Me	Ph	$S(CH_2)_3S$			(75)	810
Me	Ph	SEt	SEt		(35)	809
Ph	Ph	Cl	Cl		(56)	808
Ph	Ph	SEt	SEt		(15)	809

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

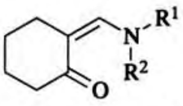
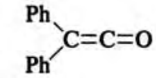
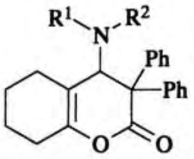
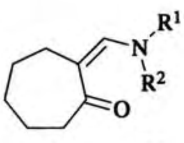
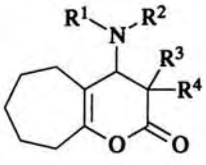
Reactant		Ketene or Ketene Source		Conditions	Product(s) and Yield(s) (%)	Refs.
		 $Ph_2C=C=O$		C_6H_6, 30 min		811
R^1	R^2					
Me	Me				(49)	
Morpholino					(53)	
Et	Et				(40)	
Piperidino					(37)	
i-Pr	*i*-Pr				(68)	
Me	Ph				(58)	
Ph	Ph				(36)	
C_8 		$R^3R^4CHCOCl$		Et_3N, C_6H_6		
R^1	R^2	R^3	R^4			
Me	Me	Cl	Cl		(59)	808
Me	Me	SEt	SEt		(42)	809
Piperidino		$S(CH_2)_3S$			(70)	810
i-Pr	*i*-Pr	Cl	Cl		(50)	808
Me	Ph	Cl	Cl		(73)	808
Me	Ph	SEt	SEt		(33)	809
Ph	Ph	Cl	Cl		(83)	808

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

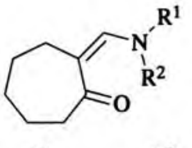
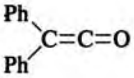
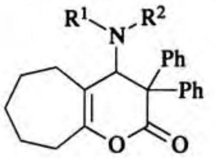
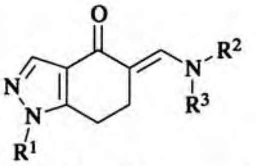
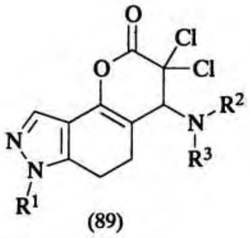
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 30 min		811
R^1 R^2				
Me Me			(59)	
Morpholino			(49)	
Et Et			(15)	
Piperidino			(43)	
i-Pr *i*-Pr			(20)	
Me Ph			(64)	
Ph Ph			(49)	
	$Cl_2CHCOCl$	Et_3N, CH_2Cl_2		812
R^1 R^2 R^3				
Me Me Me			(89)	
Me Piperidino			(49)	
Me Me Ph			(78)	
Me Ph Ph			(83)	
Ph Me Me			(67)	
Ph Piperidino			(51)	
Ph Me Ph			(90)	
Ph Ph Ph			(86)	

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

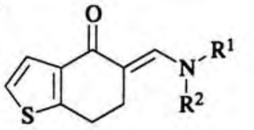
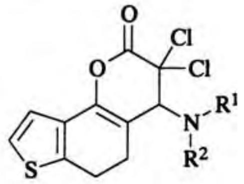
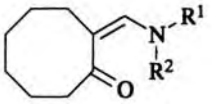
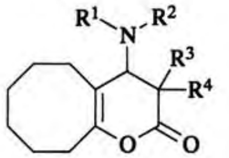
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	$Cl_2CHCOCl$	Et_3N, Et_2O		813
R^1 R^2				
$(CH_2)_2OMe$ $(CH_2)_2OMe$			(93)	
Me Ph			(84)	
Ph Ph			(98)	
	$R^3R^4CHCOCl$	Et_3N, C_6H_6		
R^1 R^2	R^3 R^4			
Me Me	Cl Cl		(46)	808
Me Me	SEt SEt		(23)	809
Morpholino	$S(CH_2)_3S$		(27)	810
Piperidino	$S(CH_2)_3S$		(40)	810
Et Et	$S(CH_2)_3S$		(52)	810
i-Pr *i*-Pr	Cl Cl		(43)	808
Me Ph	Cl Cl		(54)	808
Me Ph	$S(CH_2)_3S$		(37)	810
Me Ph	SEt SEt		(43)	809
Ph Ph	Cl Cl		(36)	808

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

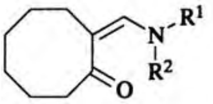
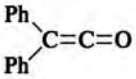
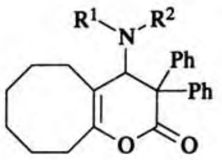
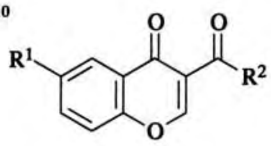
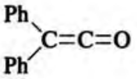
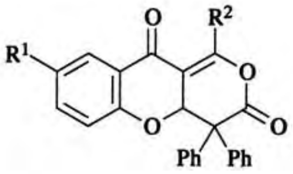
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_6, 30 min		811
R^1 R^2				
Me Me			(29)	
Morpholino			(63)	
Piperidino			(68)	
Et Et			(59)	
i-Pr *i*-Pr			(55)	
Me Ph			(86)	
Ph Ph			(50)	
C_{10}				
	 $Ph_2C=C=O$	130°		
R^1 R^2				
H H			(60)	256
Me H			(55)	256
H Ph			(—)	749, 797

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

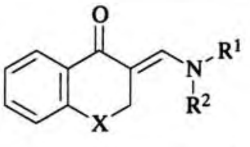
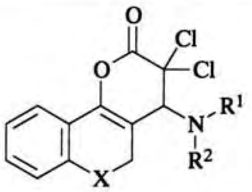
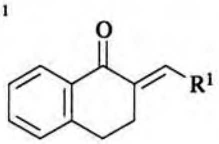
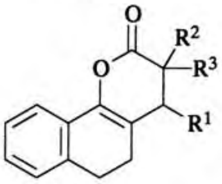
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6		
X R^1 R^2				
O Piperidino			(23)	814
O Me Ph			(79)	814
O Ph Ph			(90)	814
S *i*-Pr *i*-Pr			(81)	258
S Me Ph			(96)	258
C_{11}				
	$R^2R^3CHCOCl$	Et_3N		
R^1	R^2 R^3			
OMe	Cl Cl		(—)	327
OMe	Me Cl		(—)	327
OMe	Ph Cl		(—)	327
OMe	Ph Et		(65)	327
OMe	Ph Ph		(82)	327
N(Pr-*i*)$_2$	Cl Cl		(65)	815
N(Me)Ph	Cl Cl		(49)	815
NPh$_2$	Cl Cl		(80)	815

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

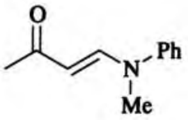
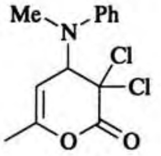
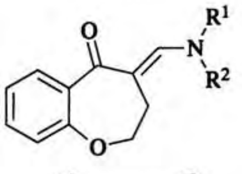
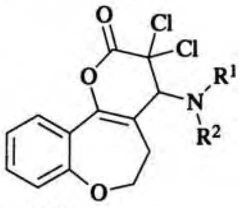
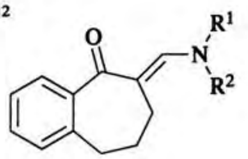
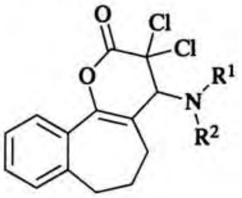
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (53)	816
 R^1 R^2 Morpholino *i*-Pr *i*-Pr Me Ph Ph Ph	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (44) (86) (70) (82)	817
C_{12}  R^1 R^2 *i*-Pr *i*-Pr Me Ph Ph Ph	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (95) (62) (78)	818

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

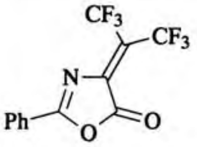
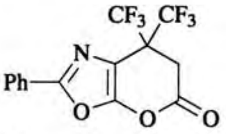
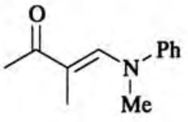
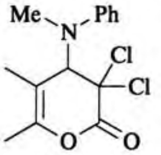
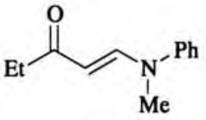
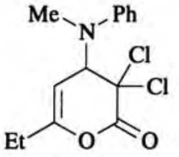
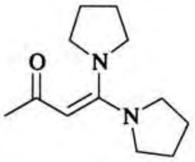
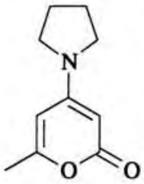
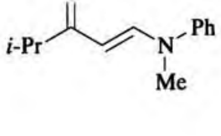
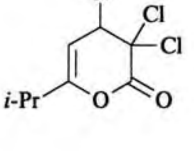
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	Et_3N, Py, -70°	 (66)	257
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (56)	816
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (77)	816
	$CH_2{=}C{=}O$	Et_2O, 0°	 (58)	259
C_{13} 	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (77)	819

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

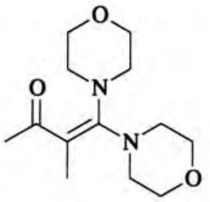
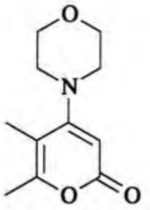
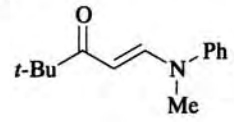
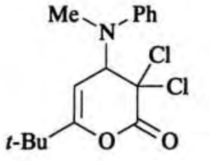
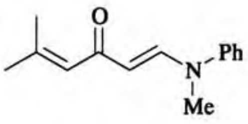
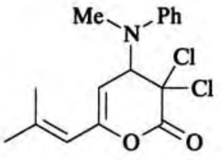
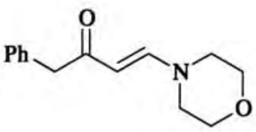
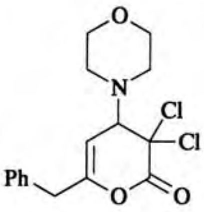
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	Et_2O, 0°	 (51)	259
C_{14}				
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (29)	819
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (45)	820
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (10)	821

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

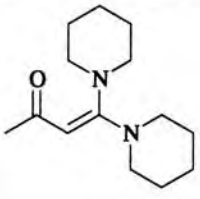
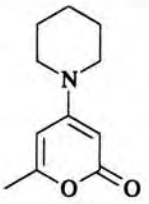
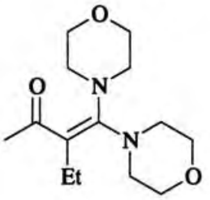
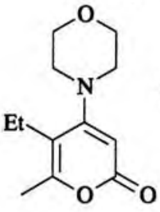
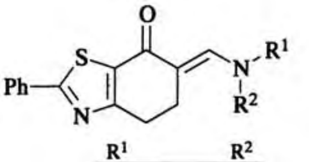
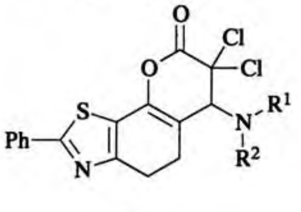
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$CH_2{=}C{=}O$	Et_2O, 0°	 (54)	259
	$CH_2{=}C{=}O$	Et_2O, 0°	 (51)	259
	$Cl_2CHCOCl$	Et_3N, C_6H_6		822
R^1 R^2				
Me Me			(87)	
Morpholino			(84)	
Et Et			(61)	
Piperidino			(67)	
i-Pr *i*-Pr			(90)	
Me Ph			(90)	
Ph Ph			(92)	

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

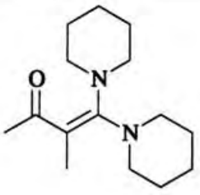
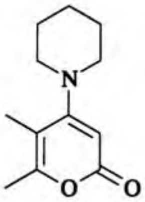
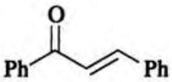
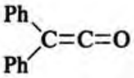
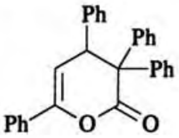
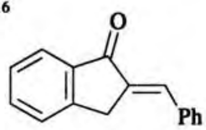
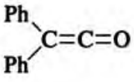
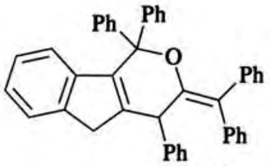
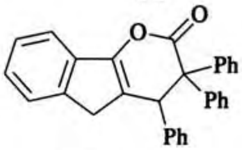
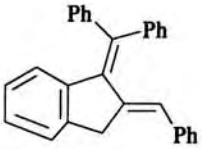
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$CH_2{=}C{=}O$	Et_2O, 0°		(55)	259
C_{15}					
	 $Ph_2C{=}C{=}O$	130-140°, 4 h		(19)	252
C_{16}					
	 $Ph_2C{=}C{=}O$	140-145°, 3.5 h		(—) +	253
				(—) +	
				(—)	

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

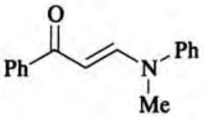
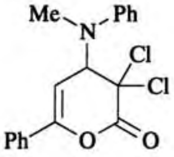
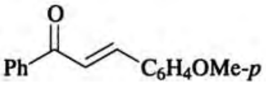
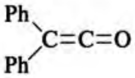
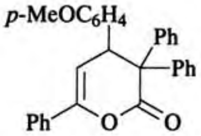
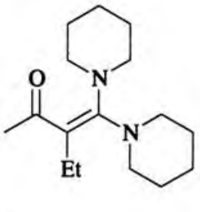
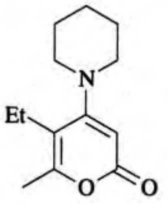
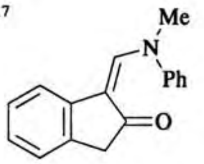
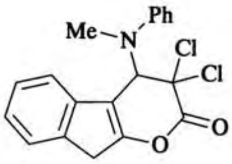
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6		(76)	823
	 $Ph_2C{=}C{=}O$	130-140°		(36)	252
	$CH_2{=}C{=}O$	Et_2O, 0°		(53)	259
C_{17}					
	$Cl_2CHCOCl$	Et_3N, C_6H_6		(58)	824

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

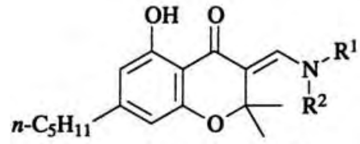
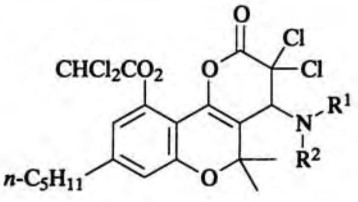
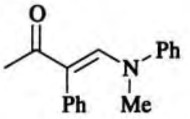
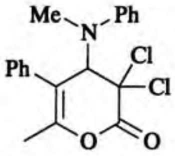
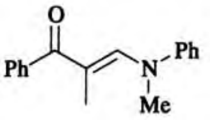
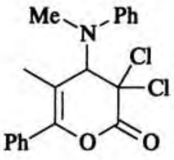
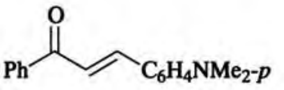
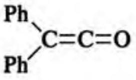
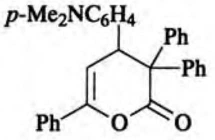
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
 R^1 R^2 Morpholino Et Et Piperidino Me Ph	$Cl_2CHCOCl$	Et_3N, Et_2O	 (68) (71) (76) (80)	825
	$Cl\ _2CHCOCl$	Et_3N, C_6H_6	 (25)	821
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (47)	826
	 $Ph_2C=C=O$	130-140°	 (46)	252

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

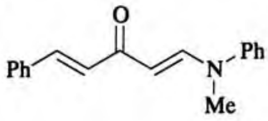
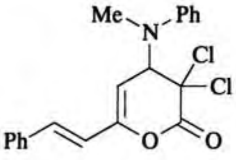
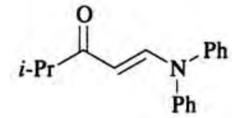
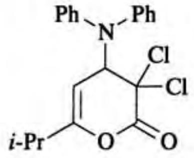
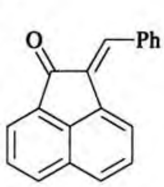
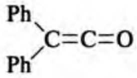
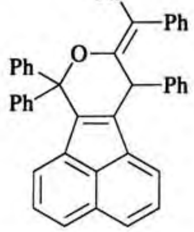
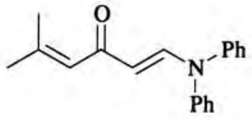
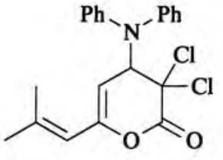
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18}				
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (82)	820
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (60)	819
C_{19}				
	 $Ph_2C=C=O$	130°, 2 h	 (—)	254
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (35)	820

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

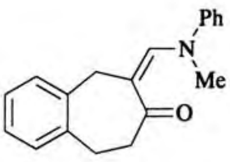
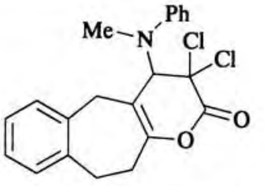
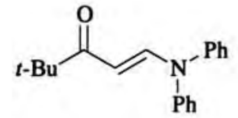
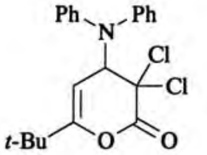
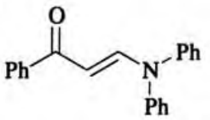
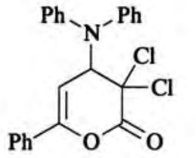
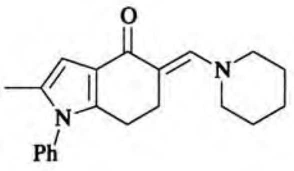
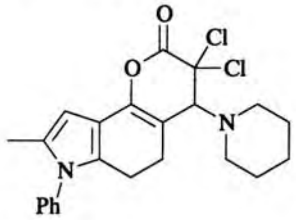
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, CH_2Cl_2	 (92)	255
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (54)	819
C_{21} 	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (45)	823
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (64)	827

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

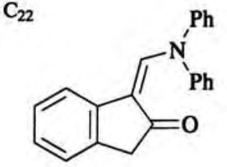
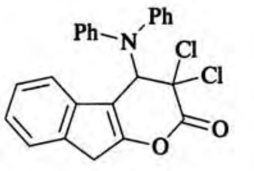
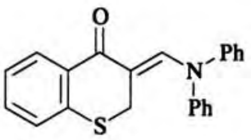
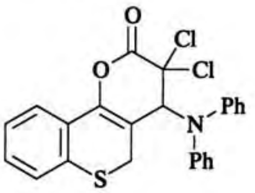
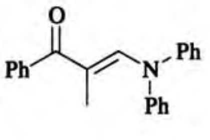
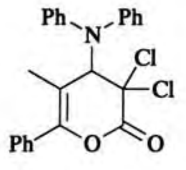
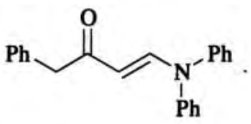
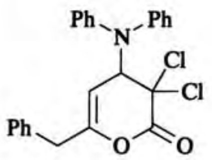
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{22} 	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (55)	824
	$Cl_2CHCOCl$	Et_3N, Et_2O	 (74)	258
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (39)	826
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (30)	821

TABLE XXXII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED CARBONYL COMPOUNDS (*Continued*)

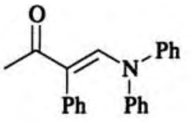
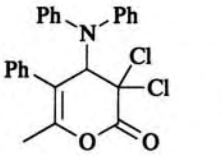
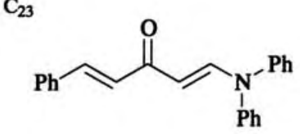
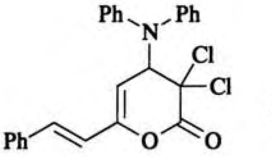
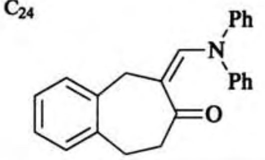
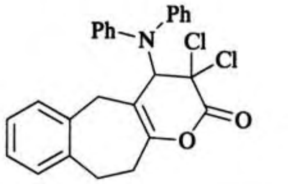
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (31)	821
C_{23} 	$Cl_2CHCOCl$	Et_3N, Et_2O	 (80)	820
C_{24} 	$Cl_2CHCOCl$	Et_3N, Et_2O	 (50)	255

TABLE XXXIII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED THIOCARBONYL COMPOUNDS

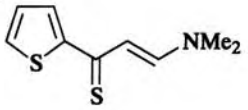
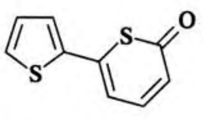
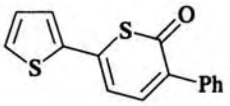
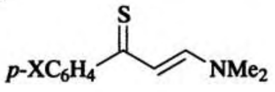
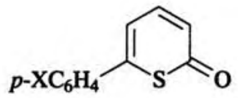
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9				
	$CH_2{=}C{=}O$	Me_2CO, 1 h	 (59)	260
	$PhCH_2COCl$	Et_3N, C_6H_6, 1 h	 (53)	260
C_{11}				
	$CH_2{=}C{=}O$	Me_2CO, 1 h		260, 261
X				
Cl			(78)	
Br			(63)	
H			(29)	
Me			(62)	
OMe			(45)	

TABLE XXXIII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED THIOCARBONYL COMPOUNDS (*Continued*)

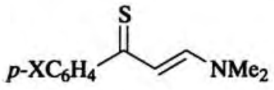
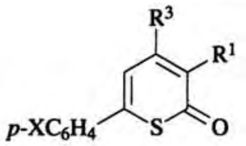
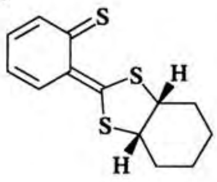
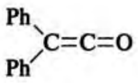
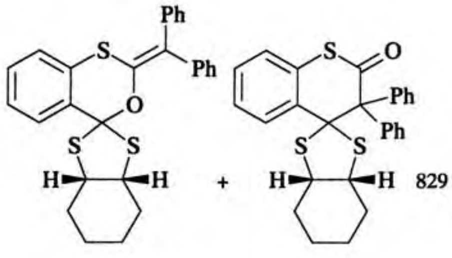
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	$R^1R^2CHCOCl$	Et_3N, C_6H_6, 1 h		
X	R^1 R^2		R^3	
Cl	Cl Cl		NMe_2 (41)	260
Cl	Ph H		H (38)	260
Br	Cl Cl		NMe_2 (24)	260
Br	Ph H		H (34)	260
H	Cl Cl		NMe_2 (18)	260
H	Ph H		H (53)	260, 828
Me	Cl Cl		NMe_2 (16)	260
Me	Ph H		H (21)	260, 828
OMe	Cl Cl		NMe_2 (20)	260
OMe	Ph H		H (23)	260, 828
C_{13}				
	 $Ph_2C{=}C{=}O$	C_6H_6, 40°	 I II I + II (73)	829

TABLE XXXIII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED THIOCARBONYL COMPOUNDS (*Continued*)

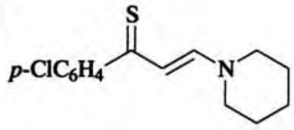
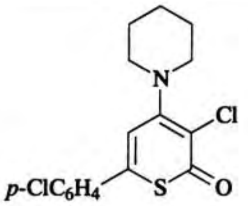
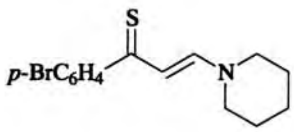
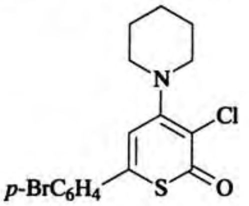
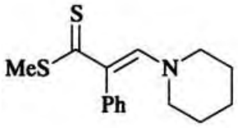
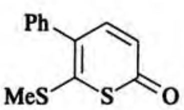
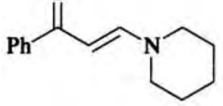
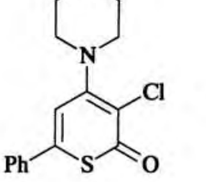
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}				
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (41)	830
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (24)	830
	$CH_2{=}C{=}O$	C_6H_6	 (73)	831
	$Cl_2CHCOCl$	Et_3N, C_6H_6	 (18)	830

TABLE XXXIII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED THIOCARBONYL COMPOUNDS (*Continued*)

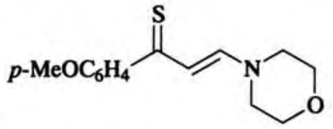
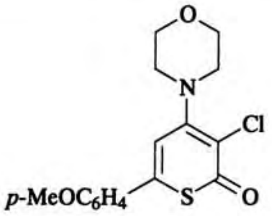
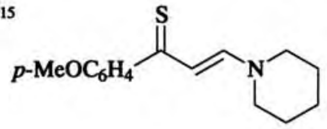
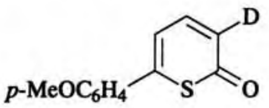
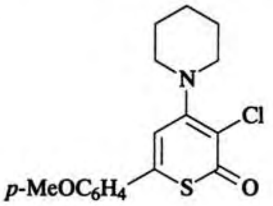
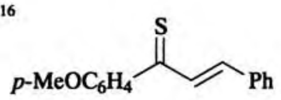
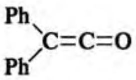
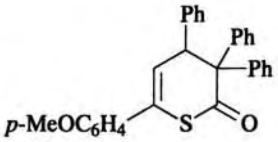
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Cl_2CHCOCl$	Et_3N, C_6H_6		(20)	830
C_{15} 	$CD_2{=}C{=}O$	Me_2CO		(—)	260
	$Cl_2CHCOCl$	Et_3N, C_6H_6		(16)	830
C_{16} 	 $Ph_2C{=}C{=}O$	C_6H_6, 80°		(11)	832

TABLE XXXIII. [4+2] CYCLOADDITION OF KETENES TO α,β-UNSATURATED THIOCARBONYL COMPOUNDS (*Continued*)

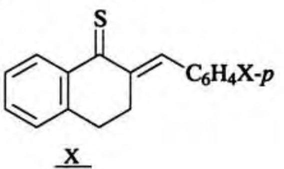
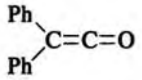
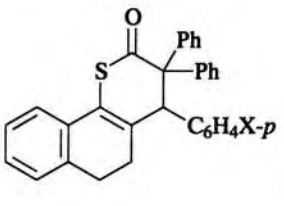
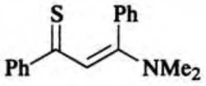
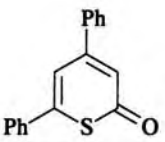
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17}  X Cl H OMe	 $Ph_2C{=}C{=}O$	C_6H_6, 80°	 (17) (51) (35)		832
	$CH_2{=}C{=}O$	—		(36)	261

TABLE XXXIV. [4+2] CYCLOADDITION OF KETENES TO ISOCYANATES AND ISOTHIOCYANATES

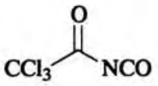
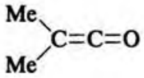
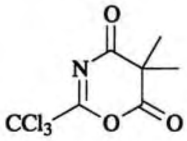
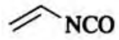
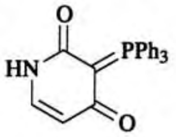
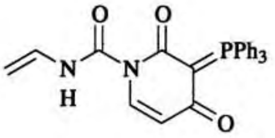
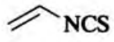
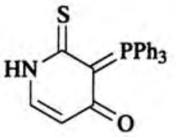
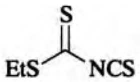
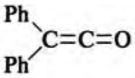
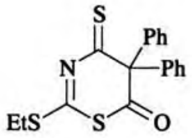
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
	 $Me_2C{=}C{=}O$	C_6H_6	 (77)	188
	$Ph_3P{=}C{=}C{=}O$	C_6H_6	 (98) +  (Tr)	266
	$Ph_3P{=}C{=}C{=}O$	C_6H_6	 (94)	266
C_4				
	 $Ph_2C{=}C{=}O$	Et_2O, 48 h	 (37)	264

TABLE XXXIV. [4+2] CYCLOADDITION OF KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

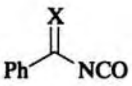
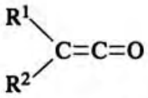
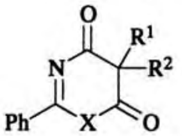
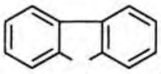
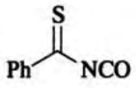
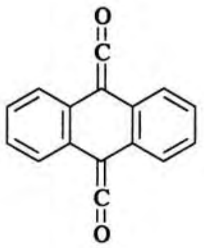
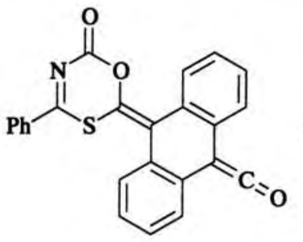
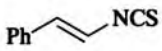
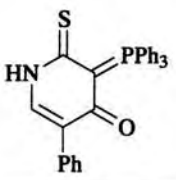
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8				
		Et_2O or PhMe		
X	R^1	R^2		
O	H	H	(51)	188
O	Me	Me	(25)	188
S			(42)	263
S	Ph	Ph	(78)	263
S	Ph	2,4,6-$Me_3C_6H_2$	(82)	263
S	Ph	1-$C_{10}H_7$	(94)	263
		C_6H_6	 (43)	263
C_9				
	$Ph_3P{=}C{=}C{=}O$	C_6H_6	 (73)	266

TABLE XXXV. [4+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS

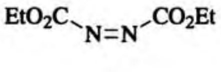
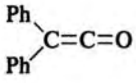
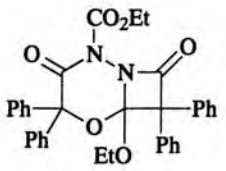
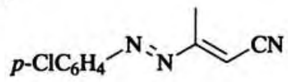
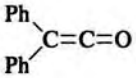
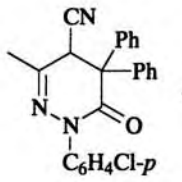
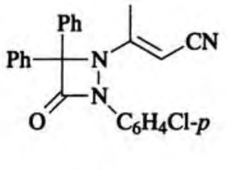
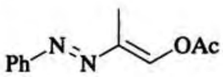
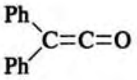
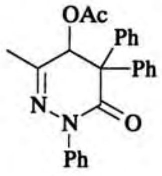
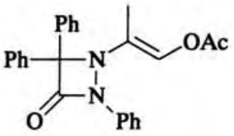
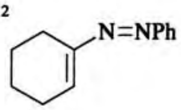
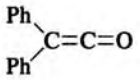
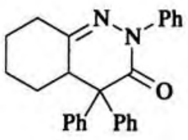
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6				
 $EtO_2CN=NCO_2Et$	 $Ph_2C=C=O$	—	 (—)	267
C_{10}				
	 $Ph_2C=C=O$	C_6H_6	 (10) +  (75)	268
C_{11}				
	 $Ph_2C=C=O$	C_6H_6	 (13) +  (46)	268
C_{12}				
	 $Ph_2C=C=O$	C_6H_6	 (72)	268

TABLE XXXV. [4+2] CYCLOADDITION OF KETENES TO AZO COMPOUNDS (*Continued*)

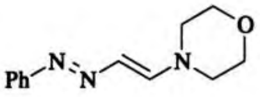
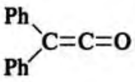
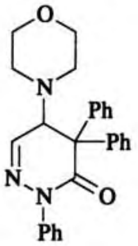
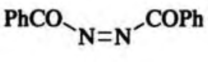
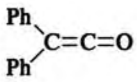
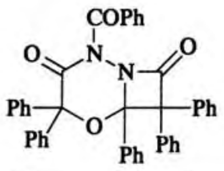
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
	 $Ph_2C=C=O$	C_6H_6	 (84)	268
C_{14}				
 $PhCON=NCOPh$	 $Ph_2C=C=O$	—	 (—)	267

TABLE XXXVI. [4+2] CYCLOADDITION OF KETENES TO THIOACYL IMINES

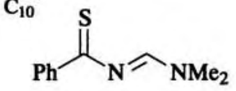
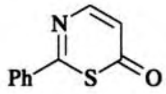
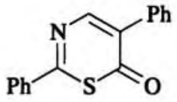
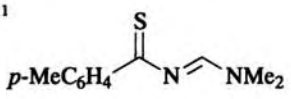
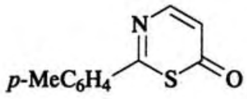
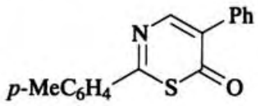
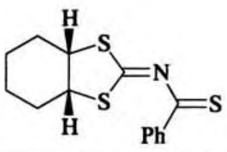
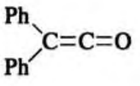
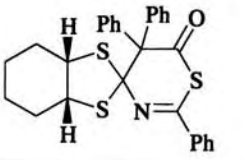
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	$CH_2{=}C{=}O$	C_6H_6	 (40)	269
	$PhCH_2COCl$	Et_3N, C_6H_6	 (22)	269
C_{11} 	$CH_2{=}C{=}O$	C_6H_6	 (40)	269
	$PhCH_2COCl$	Et_3N, C_6H_6	 (18)	269
	 $Ph_2C{=}C{=}O$	DMF, 25°	 (80)	270, 271

TABLE XXXVII. [4+2] CYCLOADDITION OF KETENES TO MESOIONIC COMPOUNDS

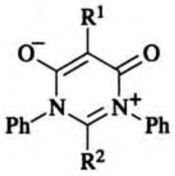
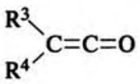
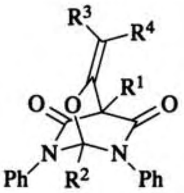
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		MeCN, 20°		272
R^1 R^2	R^3 R^4			
Me H	H H		(99)	
Me H	EtO_2C EtO_2C		(88)	
Me H	Ph Ph		(74)	
Me Me	H H		(68)	
Me Me	CF_3 CF_3		(87)	
H Ph	H H		(83)	
H Ph	Me Me		(93)	
H Ph	Ph Ph		(88)	
Me Ph	EtO_2C EtO_2C		(74)	

TABLE XXXVIII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO OLEFINS

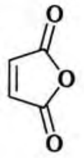
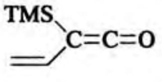
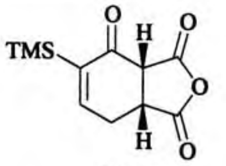
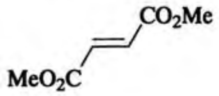
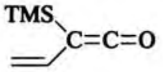
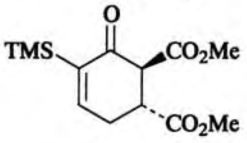
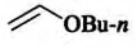
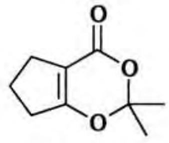
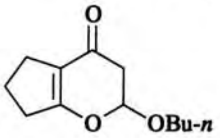
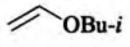
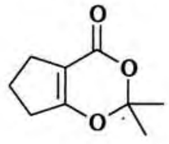
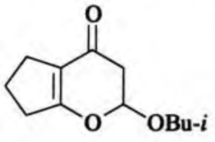
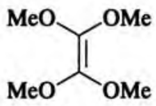
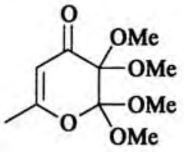
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4 		$CHCl_3$, 40°, 12 h	 (89)	273
C_6 		PhMe, 95°, 38 h	 (62)	273
		140-150°	 (74.5)	274
		120-140°	 (76)	274
	MeCOC≡COEt	Xylene, 120-140°	 (38)	282

TABLE XXXVIII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO OLEFINS (*Continued*)

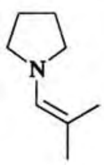
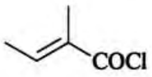
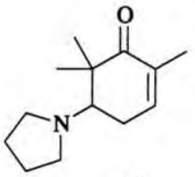
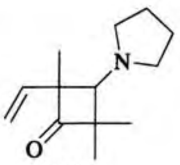
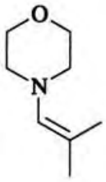
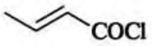
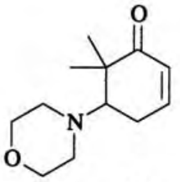
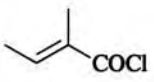
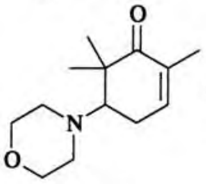
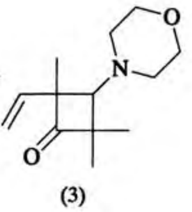
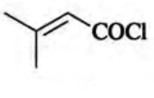
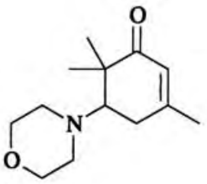
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 		Et_3N, C_6H_{14}, 70°	 (28) +  (28)	276
		Et_3N, C_6H_{14}, 70°	 (46)	276
		Et_3N, C_6H_{14}, 70°	 (23) +  (3)	276
		Et_3N, CH_2Cl_2, 25°	 (—)	276

TABLE XXXVIII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO OLEFINS (*Continued*)

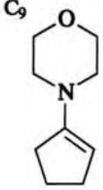
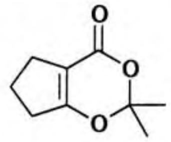
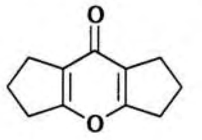
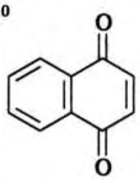
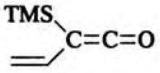
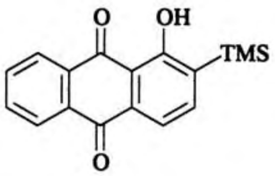
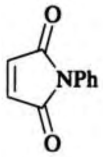
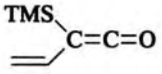
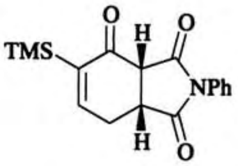
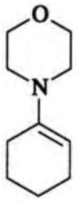
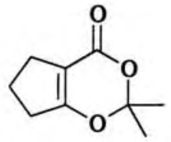
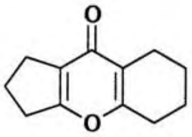
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 		140-150°	 (8)	274
C_{10} 		$CHCl_3$, 60°, 41 h	 (28)	273
		$CHCl_3$, 40°, 24 h	 (74)	273
		140-150°	 (31.5)	274

TABLE XXXIX. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO ACETYLENES

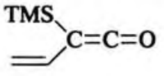
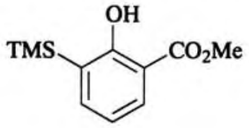
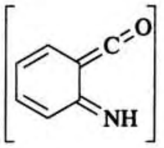
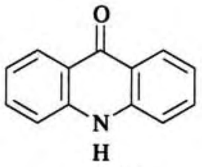
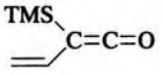
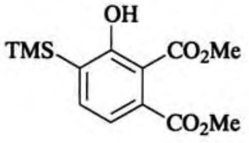
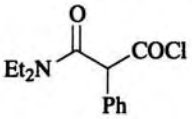
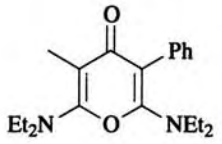
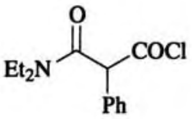
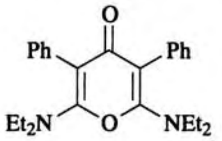
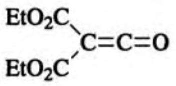
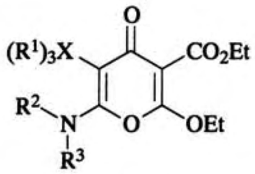
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_4					
$HC\equiv CCO_2Me$		PhMe, 95°, 63 h		(45)	273
C_6					
		240°		(—)	277
$MeO_2CC\equiv CCO_2Me$		1. $CHCl_3$, 40° 2. CF_3CO_2H		(60)	273
C_7					
$MeC\equiv CNEt_2$		Et_3N		(70)	278
$PhC\equiv CNEt_2$		Et_3N		(50)	278

TABLE XXXIX. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO ACETYLENES (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12-32}				
$(R^1)_3XC{\equiv}CNR^2R^3$	 $(EtO_2C)_2C{=}C{=}O$	Et_2O, 25°		279

X	R^1	R^2	R^3	Product(s) and Yield(s) (%)
Sn	Me	Me	Ph	(—)
Sn	Me	Ph	Ph	(—)
Si	Me	Ph	Ph	(—)
Si	Ph	Me	Me	(—)
Si	Ph	Et	Et	(—)
Sn	Ph	Me	Ph	(—)
Ge	Ph	Me	Ph	(—)
Si	Ph	Ph	Ph	(—)
Sn	Ph	Ph	Ph	(—)

TABLE XL. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO ALDEHYDES

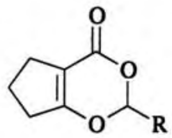
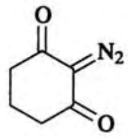
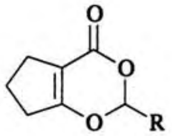
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RCHO	$ClCO(CH_2)_4COCl$	Et_3N, Et_2O, 35°, 30 min		280
R				
CCl_3			(65.6)	
CBr_3			(21)	
Et			(88.5)	
2-Furyl			(54)	
4-Pyridyl			(45)	
o-ClC_6H_4			(40)	
p-ClC_6H_4			(65)	
p-$O_2NC_6H_4$			(33)	
Ph			(71)	
o-MeC_6H_4			(61.5)	
p-MeC_6H_4			(59)	
p-$MeOC_6H_4$			(71.5)	
o-CH_2=CHC_6H_4			(53.5)	
RCHO		$HgCl_2$, xylene 130-140°		
R				
CCl_3			(66)	290
o-ClC_6H_4			(61)	290
p-ClC_6H_4p			(54)	290
p-$O_2NC_6H_4$			(74)	281, 290

TABLE XL. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO ALDEHYDES (*Continued*)

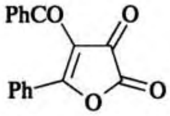
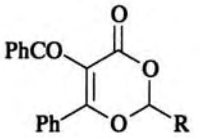
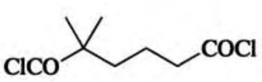
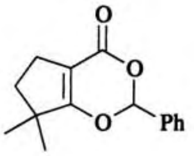
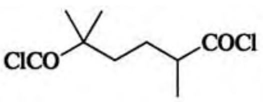
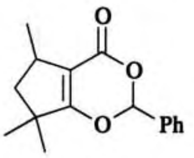
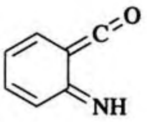
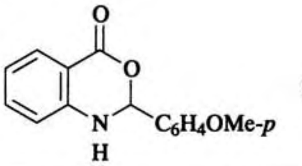
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RCHO		Xylene, 130°, -CO		833
R				
CCl_3			(74)	
3-Pyridyl			(89)	
p-ClC_6H_4			(55)	
m-$O_2NC_6H_4$			(60)	
p-MeC_6H_4			(68)	
C_7				
PhCHO		Et_3N, Et_2O	 (56)	280
		Et_3N, Et_2O	 (60)	280
C_8				
p-$MeOC_6H_4CHO$		248°	 (—)	277

TABLE XLI. [4+2] CYCLOADDITION OF ACYL KETENES TO KETONES

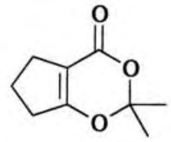
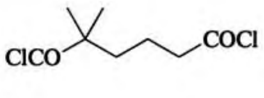
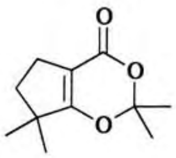
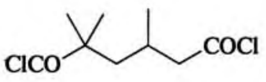
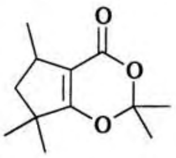
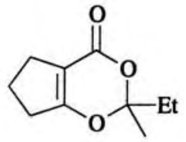
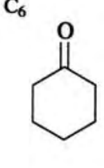
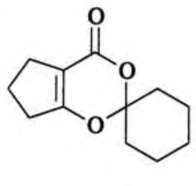
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Ref s.
C_3				
Me_2CO	$ClCO(CH_2)_4COCl$	Et_3N, Et_2O, 35°, 30 min	 (71.5)	280
		Et_3N, Et_2O, 35°, 30 min	 (85.5)	280
		Et_3N, Et_2O, 35°, 30 min	 (85)	280
C_4				
MeCOEt	$ClCO(CH_2)_4COCl$	Et_3N, Et_2O, 35°, 30 min	 (51.5)	280
C_6				
	$ClCO(CH_2)_4COCl$	Et_3N, Et_2O, 35°, 30 min	 (71)	280

TABLE XLI. [4+2] CYCLOADDITION OF ACYL KETENES TO KETONES (*Continued*)

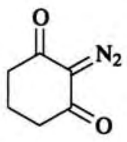
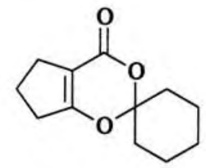
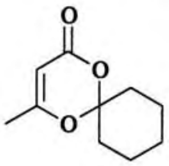
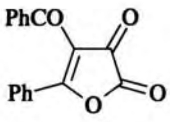
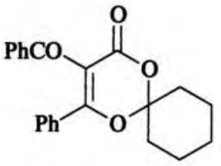
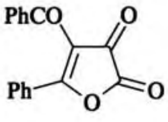
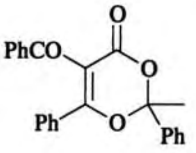
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
		HgCl$_2$, xylene, 130-140°		(72.5)	281
	MeCOC$\equiv$COEt	Xylene, 130°		(94)	282
		Xylene, 130°		(71)	833
C$_8$ MeCOPh		Xylene, 130°		(70)	833

TABLE XLI. [4+2] CYCLOADDITION OF ACYL KETENES TO KETONES (*Continued*)

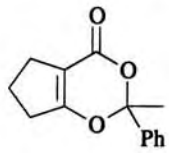
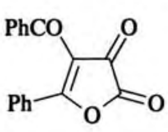
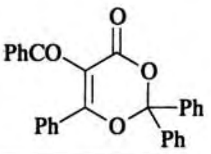
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
	ClCO(CH$_2$)$_4$COCl	Et$_3$N, Et$_2$O, 35°, 30 min		(9)	280
C$_{13}$ Ph$_2$CO		Xylene, 130°		(55)	833

TABLE XLII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO NITRILES

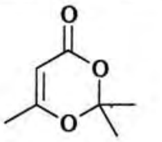
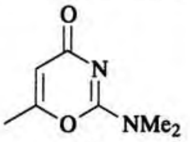
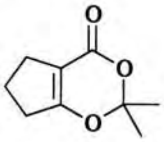
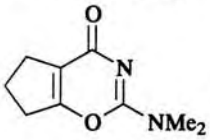
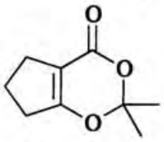
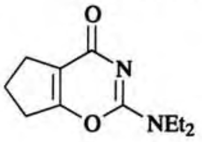
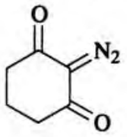
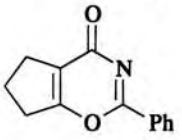
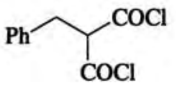
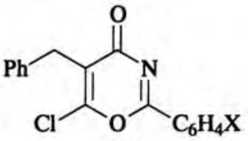
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
C_3					
Me_2NCN		120-130°		(85)	274
		120-140°		(84)	274
C_5					
Et_2NCN		120-140°		(93.5)	274
C_7					
PhCN		145-150°		(66)	281, 290
XC_6H_4CN		120-130° 25 min			283
X					
p-Cl			(29)		
o-O_2N			(22)		
H			(40)		
p-Me			(17)		
3,4-Me_2			(33)		

TABLE XLII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO NITRILES (*Continued*)

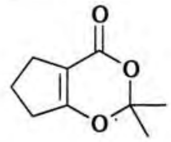
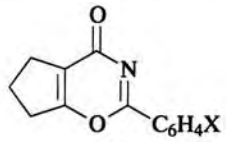
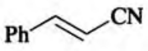
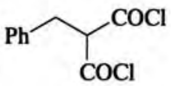
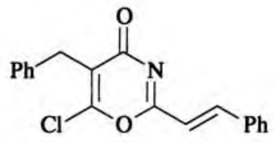
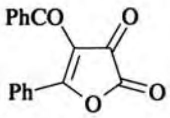
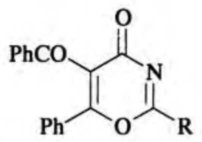
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)		Refs.
XC_6H_4CN		140-150°, 15-20 min			274
X					
H			(55)		
o-Cl			(1)		
p-Cl			(30)		
o-Me			(19)		
m-Me			(46)		
p-Me			(35)		
p-OMe			(56)		
		140°, 4 min		(5)	283
RCN		130°			834
R					
Ph			(47)		
3,4-$Me_2C_6H_3$			(44)		
1-$C_{10}H_7$			(35)		

TABLE XLIII. [4+2] CYCLOADDITION OF ACYL KETENES TO CYANATES

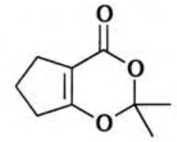
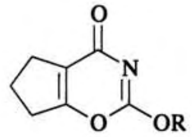
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
ROCN		Xylene, 140-150°		274
R				
2,4-$Cl_2C_6H_3$			(43)	
m-ClC_6H_4			(57)	
p-ClC_6H_4			(70.5)	
p-$O_2NC_6H_4$			(44)	
Ph			(76)	
2-Me-4-ClC_6H_3			(50.5)	
p-MeC_6H_4			(47.5)	
2,4-$Me_2C_6H_3$			(19)	
p-(*t*-Bu)C_6H_4			(37.5)	

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES

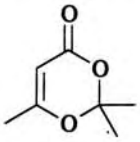
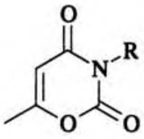
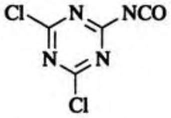
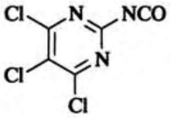
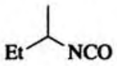
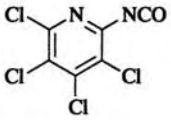
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO		Xylene, 120-130°, 15-20 min	 I	
RNCO			I	
MeNCO			(63)	274
ClC_2H_4NCO			(65)	274
EtNCO			(68)	274
$MeOCH_2NCO$			(78)	274
			(33.5)	274
i-PrNCO			(68)	274
			(55)	274
n-BuNCO			(65)	274
			(63)	274
			(57)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

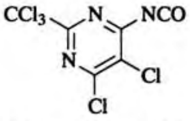
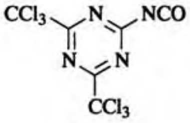
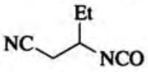
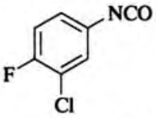
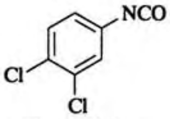
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
			(65)	274
			(73.5)	274
			(48)	274
$EtO_2C(CH_2)_2NCO$			(70)	274
			(72)	274
			(78)	274
p-FC_6H_4NCO			(76)	274
m-ClC_6H_4NCO			(72)	274
p-ClC_6H_4NCO			(85)	274
PhNCO			(68)	274
$C_6H_{11}NCO$			(52)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

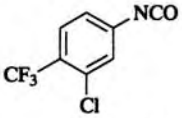
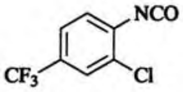
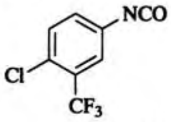
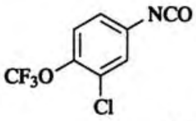
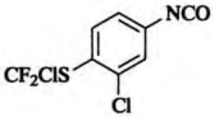
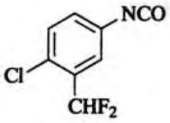
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
			(87.5)	274
			(40)	274
			(75)	274
			(78)	274
			(62)	274
			(67)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

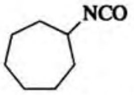
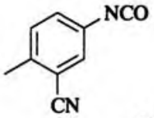
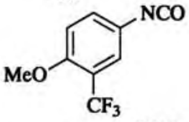
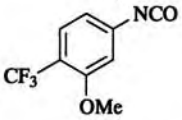
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
o-$CF_3C_6H_4NCO$			(42)	274
p-$CF_3OC_6H_4NCO$			(69)	274
m-$CF_3C_6H_4NCO$			(73)	274
p-$CF_3C_6H_4NCO$			(88)	274
m-$CHF_2C_6H_4NCO$			(60)	274
3-Cl-4-$MeOC_6H_3NCO$			(75)	274
m-MeC_6H_4NCO			(67)	274
$PhCH_2NCO$			(60)	274
p-$MeOC_6H_4NCO$			(86)	274
i-$BuO_2C(CH_2)_2NCO$			(63)	274
			(63)	274
$C_6H_{11}CH_2NCO$			(72)	274
n-$C_7H_{15}NCO$			(52)	274
			(62)	274
			(79)	274
			(52)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

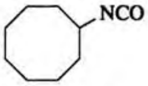
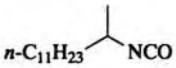
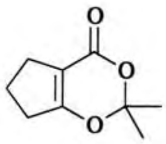
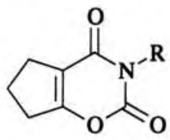
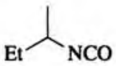
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
p-$EtOC_6H_4NCO$			(79)	274
$Ph(CH_2)_2NCO$			(65)	274
			(49)	274
			(45)	274
n-$C_{14}H_{29}NCO$			(48)	274
n-$C_{18}H_{37}NCO$			(48)	274
RNCO		Xylene, 120-140°		
RNCO			I	
Me			(70.5)	274
MeO_2CNCO			(29)	274
$Cl(CH_2)_2NCO$			(73)	274
EtNCO			(74)	274
$MeOCH_2NCO$			(54)	274
n-PrNCO			(86)	274
i-PrNCO			(78)	274
EtO_2CCH_2NCO			(68)	274
n-BuNCO			(78)	274
			(75)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

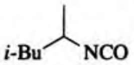
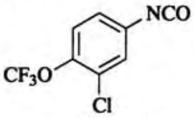
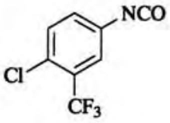
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
i-PrNCO			(82)	274
n-BuSCONCO			(12.5)	274
n-BuOCH$_2$NCO			(73)	274
3,4-Cl$_2$C$_6$H$_3$NCO			(75)	274
2,5-Cl$_2$C$_6$H$_3$NCO			(33.5)	274
2,4-Cl$_2$C$_6$H$_3$NCO			(52.5)	274
o-ClC$_6$H$_4$NCO			(64.5)	274
m-ClC$_6$H$_4$NCO			(64.5)	274
p-ClC$_6$H$_4$NCO			(65)	274
p-O$_2$NC$_6$ H$_4$NCO			(30)	274
PhNCO			(61)	274
PhNCS			(29)	274
C$_6$H$_{11}$NCO			(80)	274
Cl(CH$_2$)$_6$NCO			(68)	274
			(62)	274
			(52)	274
			(42)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

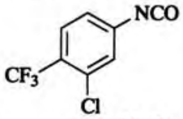
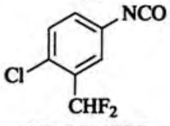
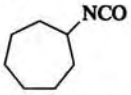
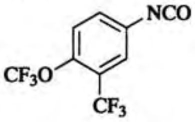
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
			(60)	274
			(40)	274
p-CF$_3$C$_6$H$_4$NCO			(78.5)	274
m-CF$_3$C$_6$H$_4$NCO			(46.5)	274
o-CF$_3$C$_6$H$_4$NCO			(46.5)	274
PhSCONCO			(57)	274
PhO$_2$CNCO			(52)	274
PhCH$_2$NCO			(89)	274
m-MeC$_6$H$_4$NCO			(61.5)	274
p-MeOC$_6$H$_4$NCO			(70)	274
			(73)	274
C$_6$H$_{11}$CH$_2$NCO			(82)	274
i-BuO$_2$C(CH$_2$)$_2$NCO			(62)	274
2,4-(CF$_3$)$_2$C$_6$H$_3$NCO			(52.5)	274
			(56.5)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

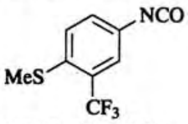
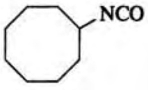
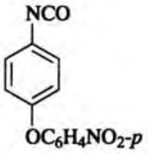
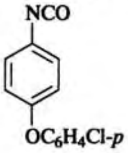
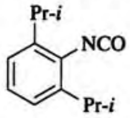
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
			(36)	274
2,6-$Me_2C_6H_3NCO$			(18.5)	274
o-EtC_6H_4NCO			(34)	274
p-$EtOC_6H_4NCO$			(71.5)	274
$Ph(CH_2)_2NCO$			(54.5	274
			(65)	274
			(45)	274
			(51)	274
			(17.5)	274

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

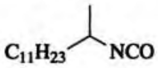
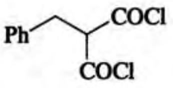
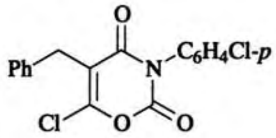
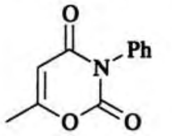
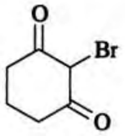
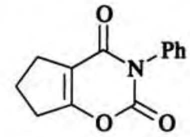
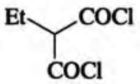
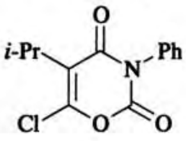
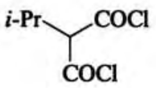
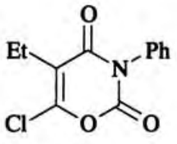
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
RNCO			I	
n-$C_{12}H_{25}NCO$			(62)	274
			(45)	274
C_7				
p-ClC_6H_4NCO		170-180°, 20 min	 (88)	283
PhNCO	MeCOC≡COEt	CCl_4, 90°, 2 h	 (41)	282
		Et_3N, C_6H_6	 (25)	284
		160-170°, 1 h	 (98)	283
		170-180°, 1 h	 (65)	283

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

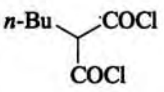
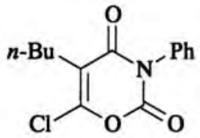
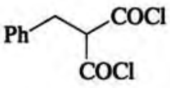
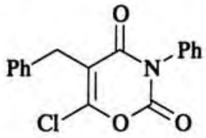
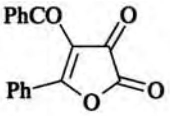
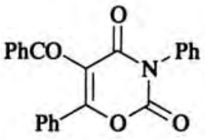
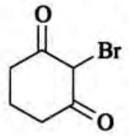
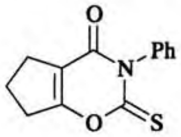
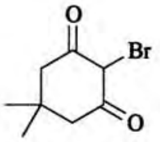
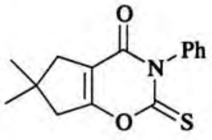
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		165°, 30 min	 (64)	283
		170-180°, 30 min	 (97)	283
PhNCS		C_6H_6, 80°	 (43)	835
		Et_3N, C_6H_6	 (12)	284
		Et_3N, C_6H_6	 (22)	284

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

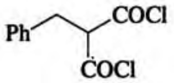
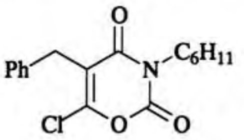
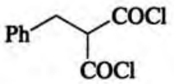
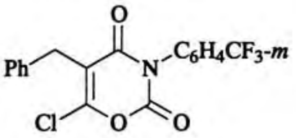
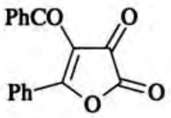
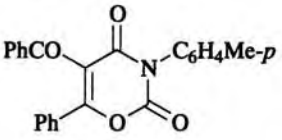
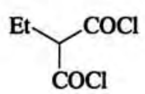
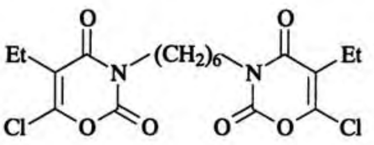
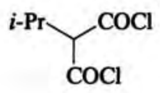
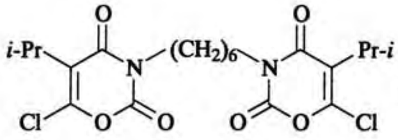
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
$C_6H_{11}NCO$		175-185°, 28 min	 (94)	283
C_8				
m-$CF_3C_6H_4NCO$		175-185°, 28 min	 (89)	283
p-MeC_6H_4NCO		C_6H_6, 80°	 (—)	835
$OCN(CH_2)_6NCO$		170-180°, 10 min	 (46)	283
		170-180°, 10 min	 (56)	283

TABLE XLIV. [4+2] CYCLOADDITION OF ACYL KETENES TO ISOCYANATES AND ISOTHIOCYANATES (*Continued*)

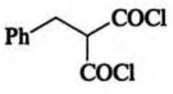
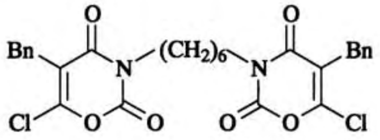
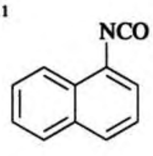
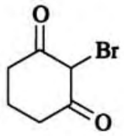
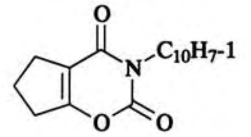
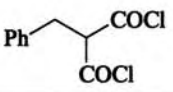
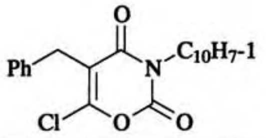
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		170-180°, 10 min	 (88)	283
C_{11} 		Et_3N, C_6H_6	 (5)	284
		180-190°	 (80)	283

TABLE XLV. [4+2] CYCLOADDITION OF ACYL KETENES TO *N*-SULFINYLAMINES

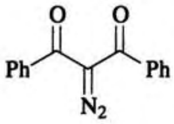
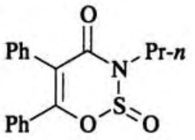
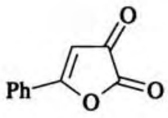
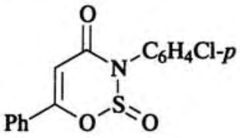
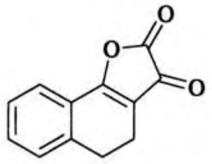
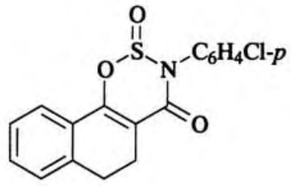
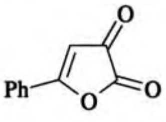
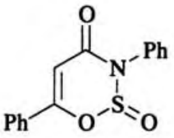
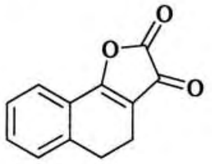
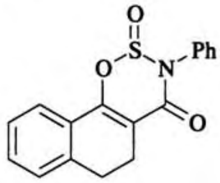
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3				
n-PrNSO		PhMe, 111°	 (20)	286
C_6				
p-ClC_6H_4NSO		C_6H_6, 80°	 (—)	287
		C_6H_6, 80°	 (—)	287
PhNSO		C_6H_6, 80°	 (49)	287
		C_6H_6, 80°	 (74)	287

TABLE XLV. [4+2] CYCLOADDITION OF ACYL KETENES TO *N*-SULFINYLAMINES (*Continued*)

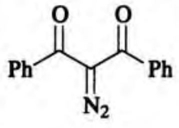
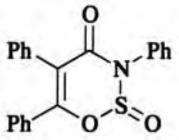
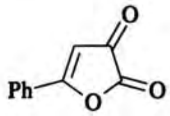
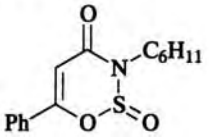
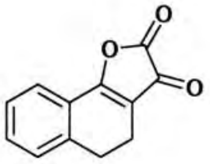
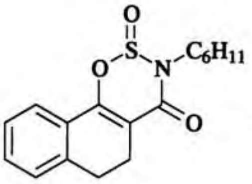
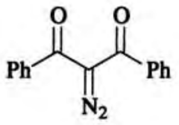
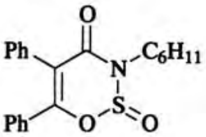
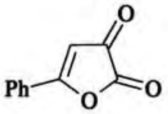
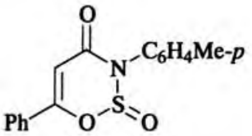
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		PhMe, 111°	 (38)	286
$C_6H_{11}NSO$		C_6H_6, 80°	 (—)	287
		C_6H_6, 80°	 (—)	287
		PhMe, 111°	 (34)	286
C_7 p-MeC_6H_4NSO		C_6H_6, 80°	 (—)	287

TABLE XLV. [4+2] CYCLOADDITION OF ACYL KETENES TO *N*-SULFINYLAMINES (*Continued*)

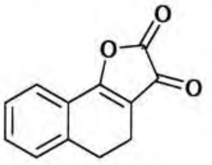
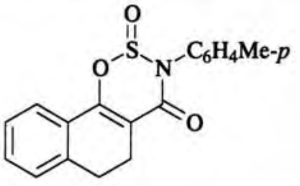
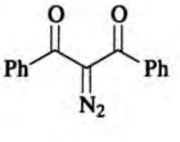
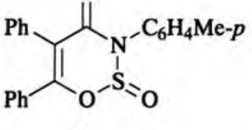
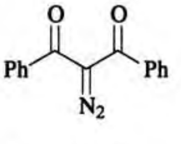
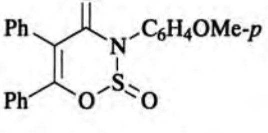
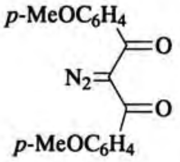
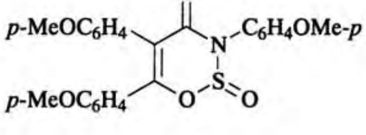
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
		C_6H_6, 80°	 (—)	287
		PhMe, 111°	 (30)	286
p-$MeOC_6H_4NSO$		PhMe, 111°	 (29)	286
		PhMe, 111°	 (16)	286

TABLE XLV. [4+2] CYCLOADDITION OF ACYL KETENES TO *N*-SULFINYLAMINES (*Continued*)

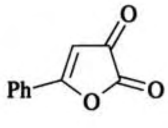
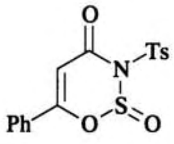
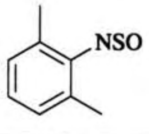
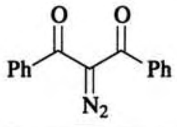
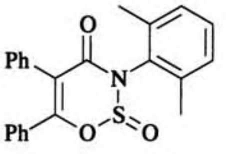
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
TsNSO		C_6H_6, 80°	 (—)	287
C_8 		PhMe, 111°	 (18)	286

TABLE XLVI. [4+2] CYCLOADDITION OF ACYL KETENES TO CARBODIIMIDES

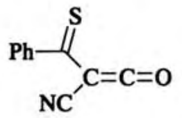
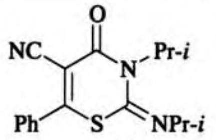
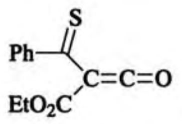
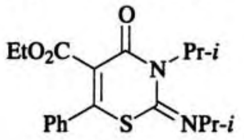
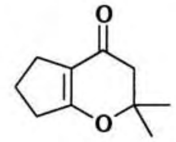
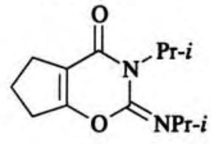
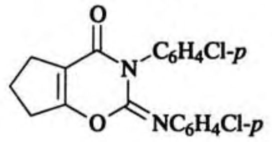
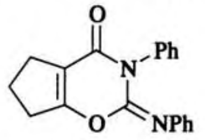
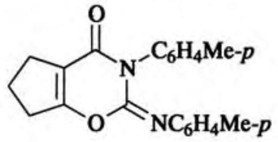
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7				
i-PrN=C=NPr-i		—	 (—)	285
		—	 (—)	285
		Xylene, 120-140°	 (76)	274
C_{13}				
p-ClC$_6$H$_4$N=C=NC$_6$H$_4$Cl-p	"	"	 (80)	274
PhN=C=NPh	"	"	 (93)	274
C_{15}				
p-MeC$_6$H$_4$N=C=NC$_6$H$_4$Me-p	"	"	 (72)	274

TABLE XLVII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO IMINES AND AZO COMPOUNDS

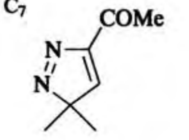
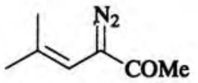
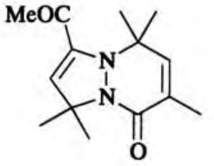
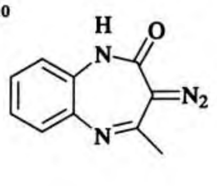
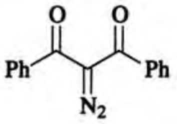
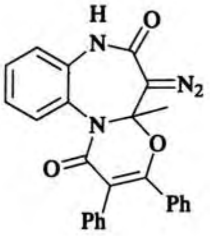
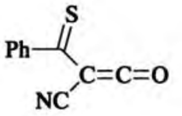
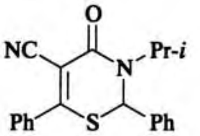
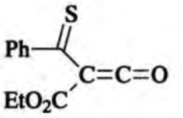
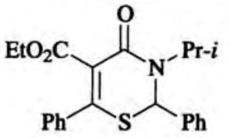
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 		hν	 (46)	288
C_{10} 		Xylene, 120°	 (72)	291
PhCH=NPr-*i*		—	 (—)	285
		—	 (—)	285

TABLE XLVII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO IMINES AND AZO COMPOUNDS (*Continued*)

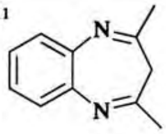
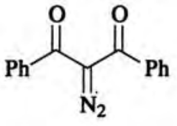
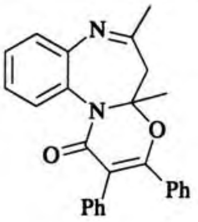
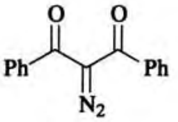
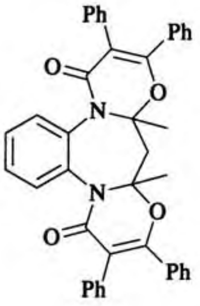
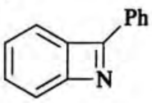
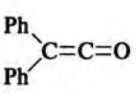
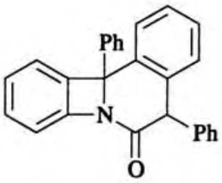
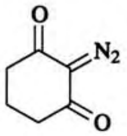
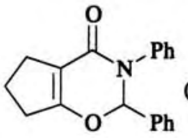
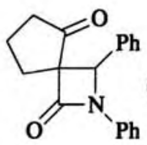
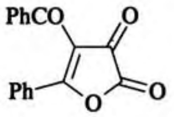
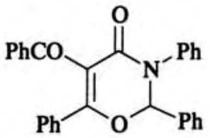
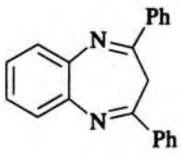
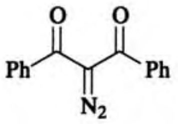
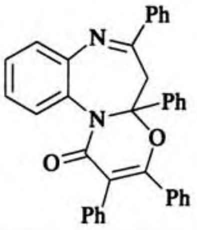
Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11} 		Xylene, 120°	 (44)	291
		Excess ketene, xylene, 120°	 (66)	291
C_{13} 	 $Ph_2C=C=O$	CH_2Cl_2	 (30)	289

TABLE XLVII. [4+2] CYCLOADDITION OF ACYL AND VINYL KETENES TO IMINES AND AZO COMPOUNDS (*Continued*)

Reactant	Ketene or Ketene Source	Conditions	Product(s) and Yield(s) (%)	Refs.
PhCH=NPh		Xylene, 140-145°	 (25) +  (17)	281, 290
		Xylene, 130°	 (27)	836
		Xylene, 120°	 (54)	291

6. Acknowledgments

The authors wish to thank the management of the Research Laboratories, Eastman Chemical Company, for their support in the preparation of this review. JAH in particular thanks Lois Epley, Debra Bledsoe, Delta Childress, Betty Hicks, Martha Yonce, and Paula Phillips for their excellent efforts in preparation of the manuscript. Both authors are grateful to Dr. R. H. Hasek, whose compilations of ketene literature in these laboratories provided a sound basis for starting the present work.

References

1. Chick, F.; Wilsmore, N. T. M. J. Chem. Soc. 1908, 946.
2. Staudinger, H.; Klever, H. W. Ber. 1908, **41**, 594.
3. Staudinger, H.; Klever, H. W. Ber. 1908, **41**, 1516, cited in C.A. 1908, **2**, 2224.
4. Staudinger, H. *Die Ketene*, Verlag von Ferdinand Enke, Stuttgart, 1912.
5. Ghosez, L.; Montaigne, R.; Mollet, P. Tetrahedron Lett. 1966, 135.
6. Stevens, H. C.; Reich, D. A.; Brandt, D. R.; Fountain, K. R.; Gaughan, E. J. J. Am. Chem. Soc. 1965, **87**, 5257.
7. Brady, W. T.; Liddell, H. G.; Vaughn, W. L. J. Org. Chem. 1966, **31**, 626.
8. Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*, Academic, New York, 1971.
9. Luknitskii, F. I.; Vovsi, B. A. Russ. Chem. Rev. (Engl. Transl.) 1969, **38**, 487.
10. Seikaly, H. R.; Tidwell, T. T. Tetrahedron 1986, **42**, 2587.
11. Scheeren, J. W. Recl. Trav. Chim. Pays-Bas 1986, **105**, 71.
12. Holder, R. W. J. Chem. Educ. 1976, **53**, 81.
13. Hasek, R. H. in *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed., Grayson, M., Eckroth, D., Eds., Vol. **13**, Wiley, New York, 1981, p. 874.
14. Roberts, J. D.; Sharts, C. M. Org. React. 1962, **12**, 1.
15. Miller, R.; Claudio, A.; Adel, S. in *Ullmann's Encyclopedia of Industrial Chemistry*, Elvers, B., Hawkins, S., Schulz, G., Eds., Vol. **A15**, VCH Verlagsgesellschaft, Weinheim, Germany, 1990, p. 63.
16. Ziegler, E. Chimia 1970, **24**, 62.
17. Quadbeck, G. Angew. Chem. 1956, **68**, 361.
18. Ulrich, H. *Cycloaddition Reactions of Heterocumulenes*, Academic, New York, 1967.
19. Brady, W. T. Tetrahedron 1981, **37**, 2949.
20. Brady, W. T. Synthesis 1971, 415.
21. Snyder, E. I. J. Org. Chem. 1970, **35**, 4287.
22. Cheburkov, Y. A.; Knunyants, I. L. Fluorine Chem. Rev. 1967, **1**, 107.
23. Moore, H. W.; Gheorghiu, M. D. Chem. Soc. Rev. 1981, 289.
24. Reisig, H. Nachr. Chem. Tech. Lab. 1986, **34**, 880.
25. Snider, B. B. Chem. Rev. 1988, **88**, 793.
26. Moore, H. W.; Decker, O. H. Chem. Rev. 1986, **86**, 821.
27. Manhas, M. S.; Bose, A. K. *Synthesis of Penicillin, Cephalosporin C. and Analogs* Marcel Dekker, New York, 1969.

28. Morin, R. B.; Gorman, M. *Chemistry and Biology of beta-Lactam Antibiotics*, Vols. **1** and **2**, Academic, New York, 1982.
29. Schaumann, E.; Kettcham, R. Angew. Chem., Int. Ed. Engl. 1982, **21**, 225.
30. Ranganathan, S.; Ranganathan, D., Mehrotra, A. K. Synthesis 1977, 289.
31. Houk, K. N. Acc. Chem. Res. 1975, **8**, 361.
32. Gompper, R. Angew. Chem., Int. Ed. Engl. 1969, **8**, 312.
33. Belluš, D.; Ernst, B. Angew. Chem., Int. Ed. Engl. 1988, **27**, 797.
34. Wong, H. N. C.; Lau, K.; Tam, K. in *Topics in Current Chemistry*, Vol. **133**, Springer-Verlag, Berlin, 1986, p. 83.
35. Trost, B. M. in *Topics in Current Chemistry*, Vol. **133**, Springer-Verlag, Berlin, 1986, p. 3.
36. Huisgen, R.; Otto, P. Tetrahedron Lett. 1968, 4491.
37. Isaacs, N. S.; Stanbury, P. F. J. Chem. Soc., Chem. Commun. 1970, 1061.
38. Rey, M.; Roberts, S.; Dieffenbacher, A.; Dreiding, A. S. Helv. Chim. Acta 1970, **53**, 417.
39. Taylor, E. C.; McKillop, A.; Hawks, H. H. *Org. Synth. Coll. Vol. VI*, Wiley, New York, 1988, p. 549.
40. Al-Husaini, A. H.; Moore, H. W. J. Org. Chem. 1985, **50**, 2595.
41. Moore, H. W.; Wilbur, D. S. J. Am. Chem. Soc. 1978, **100**, 6523.
42. Huisgen, R.; Mayr, H. Tetrahedron Lett. 1975, 2969.
43. Moore, H. W.; Wilbur, D. S. J. Org. Chem. 1980, **45**, 4483.
44. Wagner, H. U.; Gompper, R. Tetrahedron Lett. 1970, 2819.
45. Huisgen, R.; Mayr, H. Tetrahedron Lett. 1975, 2965.
46. Rey, M.; Roberts, S. M.; Dreiding, A. S.; Roussel, A.; Vanlierde, H.; Toppet, S.; Ghosez, L. Helv. Chim. Acta 1982, **65**, 703.
47. Huisgen, R.; Feiler, L. A.; Binsch, G. Chem. Ber. 1969, **102**, 3460.
48. Huisgen, R.; Feiler, L. A.; Otto, P. Tetrahedron Lett. 1968, 4485.
49. Huisgen, R.; Otto, P. J. Am. Chem. Soc. 1968, **90**, 5342.
50. Baldwin, J. E.; Kapecki, J. A. J. Am. Chem. Soc. 1969, **91**, 3106.
51. Baldwin, J. E.; Kapecki, J. A. J. Am. Chem. Soc. 1970, **92**, 4874.
52. Holder, R. W.; Graf, N. A.; Duesler, E.; Moss, J. C. J. Am. Chem. Soc. 1983, **105**, 2929.
53. Katz, T. J.; Dessau, R. J. Am. Chem. Soc. 1963, **85**, 2172.
54. Collins, C. J.; Benjamin, B. M.; Kabalka, G. W. J. Am. Chem. Soc. 1978, **100**, 2570.
55. Becker, D.; Brodsky, N. C. J. Chem. Soc., Chem. Commun. 1978, 237.

56. Hanford, W. E.; Sauer, J. C. Org. React. 1946, **3**, 108.
57. Montaigne, R.; Ghosez, L. Angew. Chem., Int. Ed. Engl. 1968, **7**, 221.
58. Kende, A. S. Tetrahedron Lett. 1967, 2661.
59. Tenud, L.; Weilenmann, M.; Dallwigk, E. Helv. Chim. Acta 1977, **60**, 975.
60. Krebs, A.; Kimling, H. Justus Liebigs, Ann. Chem. 1974, 2074.
61. Das, H.; Kooyman, E. C. Recl. Trav. Chim. Pays-Bas 1965, **84**, 965.
62. Pregaglia, G. F.; Mazzanti, G.; Binaghi, M. Makromol. Chem. 1966, **48**, 234.
63. Ashworth, G.; Berry, D.; Smith, D. C. C. J. Chem. Soc., Perkin Trans. 1 1979, 2995.
64. Berchtold, G. A.; Harvey, G. R.; Wilson, G. E. J. Org. Chem. 1961, **26**, 4776.
65. England, D. C.; Krespan, C. G. J. Am. Chem. Soc. 1966, **88**, 5582.
66. Cheburkov, Y. A.; Aronov, Y. E.; Mirzabekyants, N. S.; Knunyants, I. L. Bull. Acad. Sci USSR, Div. Chem. Sci. 1966, 745 [C.A. 1966, **65**, 8755e].
67. Cheburkov, Y. A.; Bargamova, M. D.; Knunyants, I. L. Bull. Acad. Sci USSR, Div. Chem. Sci. 1967, 2052 [C.A. 1966, **64**, 17411b].
68. Moore, H. W.; Duncan, W. G. J. Org. Chem. 1973, **38**, 156.
69. Newman, M. S.; Zuech, E. A. J. Org. Chem. 1962, **27**, 1436.
70. Ruden, R. A. J. Org. Chem. 1974, **39**, 3607.
71. Farnum, D. G.; Johnson, J. R.; Hess, R. E.; Marshall, T. B.; Webster, B. J. Am. Chem. Soc. 1965, **87**, 5191.
72. Wasserman, H. H.; Hearn, M. J.; Cochoy, R. E. J. Org. Chem. 1980, **45**, 2874.
73. Brady, W. T.; Ting, P. L. J. Org. Chem. 1975, **40**, 3417.
74. Andreades, S.; Carlson, H. D. Org. Synth. Coll. Vol. V, 1973, 679.
75. McMurry, J. E.; Miller, D. D. Tetrahedron Lett. 1983, **24**, 1885.
76. Erden, I.; de Meijere, A. Tetrahedron Lett. 1983, **24**, 3811.
77. Becker, K. B.; Labhart, M. P. Helv. Chim. Acta 1983, **66**, 1090.
78. Donskaya, N. A.; Bessmertnykh, A. G.; Drobysh, V. A.; Shabarov, Y. S. Zh. Org. Khim. 1987, **23**, 745 [C.A. 1988, **108**, 74843x].
79. Aue, D. H.; Helwig, G. S. J. Chem. Soc. Chem. Commun. 1975, 604.
80. Baldwin, J. E.; Johnson, D. S. J. Org. Chem. 1975, **38**, 2147.
81. Huisgen, R.; Koppitz, P. Chem.-Ztg. 1974, **98**, 461 [C.A. 1975, **82**, 43079t].
82. Deprés, J. P.; Coelho, F.; Greene, A. E. J. Org. Chem. 1985, **50**, 1972.
83. Greene, A. E.; Deprés, J. P. J. Am. Chem. Soc. 1979, **101**, 4003.

84. England, D. C.; Krespan, C. G. J. Org. Chem. 1970, **35**, 3300.
85. Cheburkov, Y. A.; Mukhamadaliev, N.; Knunyants, I. L. Bull. Acad. Sci USSR, Div. Chem. Sci. 1967, 361 [C.A. 1968, **68**, 59149n].
86. Clennan, E. L.; Lewis, K. K. J. Am. Chem. Soc. 1987, **109**, 2475.
87. Vogel, E.; Müller, K. Justus Liebigs Ann. Chem. 1958, **615**, 29.
88. Corey, E. J.; Ravindranathan, T. Tetrahedron Lett. 1971, 4753.
89. Corey, E. J.; Arnold, Z.; Hutton, J. Tetrahedron Lett. 1970, 307.
90. Corey, E. J.; Nicolaou, K. C.; Beames, D. J. Tetrahedron Lett. 1974, 2439.
91. Corey, E. J.; Mann, J. J. Am. Chem. Soc. 1973, **95**, 6832.
92. Stadler, H.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1984, **67**, 1854.
93. Bertrand, M.; Maurin, R.; Gras, J. L.; Gil, G. Tetrahedron 1975, **31**, 849.
94. Duncan, W. G.; Weyler, W.; Moore, H. W. Tetrahedron Lett. 1973, 4391.
95. Bampfield, H. A.; Brook, P. R.; McDonald, W. S. J. Chem. Soc., Chem. Commun. 1975, 132.
96. Hünig, S.; Buysch, H.; Hoch, H.; Lendle, W. Chem. Ber. 1967, **100**, 3996.
97. Berge, J. M.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1982, **65**, 2230.
98. Berchtold, G. A.; Harvey, G. R.; Wilson, G. E. J. Org. Chem. 1965, **30**, 2642.
99. Feiler, L. A.; Huisgen, R. Chem. Ber. 1969, **102**, 3428.
100. Martin, J. C. U.S. Patent 3,328,392, 1967.
101. Aben, R. W.; Scheeren, H. W. J. Chem. Soc., Perkin Trans. 1 1980, 3132.
102. Raynolds, P. W.; DeLoach, J. A. J. Am. Chem. Soc. 1984, **106**, 4566.
103. Huisgen, R.; Feiler, L. A.; Otto, P. Chem. Ber. 1969, **102**, 3405.
104. Brady, W. T.; Lloyd, R. M. J. Org. Chem. 1979, **44**, 2560.
105. Scarpati, R.; Sica, D. Gazz. Chim. Ital. 1967, **97**, 1073 [C.A. 1967, **67**, 63990b].
106. Hoffmann, R. W.; Bressel, U.; Gehlhaus, J.; Häuser, H. Chem. Ber. 1971, **104**, 873.
107. Snider, B. B.; Allentoff, A. J.; Kulkarni, Y. S. J. Org. Chem. 1988, **53**, 5320.
108. Lee, S. Y.; Kulkarni, Y. S.; Burbaum, B. W.; Johnston, M. I.; Snider, B. B. J. Org. Chem. 1988, **53**, 1848.
109. Kulkarni, Y. S.; Niwa, M.; Ron, E.; Snider, B. B. J. Org. Chem. 1987, **52**, 1568.
110. Snider, B. B.; Ron, E.; Burbaum, B. W. J. Org. Chem. 1987, **52**, 5413.
111. Hassner, A.; Dillon, J. Synthesis 1979, 689.

112. Danheiser, R. L.; Savariar, S. Tetrahedron Lett. 1987, **28**, 3299.

113. Hassner, A.; Dilon, J. L. J. Org. Chem. 1983, **48**, 3382.

114. Fishbein, P. L.; Moore, H. W. J. Org. Chem. 1985, **50**, 3226.

115. Hasek, R. H.; Gott, P. G.; Martin, J. C. J. Org. Chem. 1964, **29**, 2510.

116. Ammann, A.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1987, **70**, 321.

117. Chow, K.; Moore, H. W. Tetrahedron Lett. 1987, **28**, 5013.

118. Smith, L. I.; Hoehn, H. H. J. Am. Chem. Soc. 1939, **61**, 2619.

119. Smith, L. I.; Hoehn, H. H. J. Am. Chem. Soc. 1941, **63**, 1180.

120. Danheiser, R. L.; Sard, H. Tetrahedron Lett. 1983, **24**, 23.

121. Zaitseva, G. S.; Livantsova, L. I.; Baukov, Y. I.; Lutsenko, I. F. Zh. Obshch. Khim. 1984, **54**, 1323 [C.A. 1984, **101**, 171389s].

122. Hong, P.; Sonogashira, K.; Hagihara, N. J. Organomet. Chem. 1981, **219**, 363.

123. Martin, J. C. British UK Patent GB 1,049,326 [C.A. 1967, **66**, 29592t].

124. Martin, J. C. U.S. Patent 3,288,854 [C.A. 1967, **66**, 37502d].

125. Hasek, R. H.; Martin, J. C. J. Org. Chem. 1962, **27**, 3743.

126. Wasserman, H. H.; Dehmlow, E. V. Tetrahedron Lett. 1962, 1031.

127. Wasserman, H. H.; Piper, J. U.; Dehmlow, E. V. J. Org. Chem. 1973, **38**, 1451.

128. McCarney, C. C.; Ward, R. S.; Roberts, D. W. Tetrahedron 1976, **32**, 1189.

129. Nieuwenhuis, J.; Arens, J. F. Recl. Trav. Chim. Pays-Bas 1958, **77**, 761.

130. Pericas, M.; Serratosa, F. Tetrahedron Lett. 1977, 4437.

131. Danheiser, R. L.; Gee, S. K. J. Org. Chem. 1984, **49**, 1672.

132. Nieuwenhuis, J.; Arens, J. F. Recl. Trav. Chim. Pays-Bas 1958, **77**, 1153.

133. England, D. C.; Krespan, C. G. J. Org. Chem. 1970, **35**, 3312.

134. Teufel, H.; Jenny, E. F. Tetrahedron Lett. 1971, 1769.

135. Barton, D. H.; Gardner, J. N.; Petterson, R. C.; Stamm, O. A. Proc. Chem. Soc. 1962, 21 [C.A. 1962, **57**, 685d].

136. Jenny, E. F.; Schenker, K.; Woodward, R. B. Angew. Chem. 1961, **73**, 756.

137. Barton, D. H.; Gardner, J. N.; Petterson, R. C.; Stamm, O. A. J. Chem. Soc. 1962, 2708.

138. Druey, J.; Jenny, E. F.; Schenker, K.; Woodward, R. B. Helv. Chim. Acta 1962, **45**, 600.

139. Delaunois, M.; Ghosez, L. Angew, Chem., Int. Ed. Engl. 1969, **8**, 72.

140. Himbert, G. Justus Liebigs Ann. Chem. 1979, 829.

141. Himbert, G. Justus Liebigs Ann. Chem. 1979, 1828.

142. Himbert, G.; Henn, L. Z. Naturforsch. 1981, **36b**, 218.

143. Dotz, K. H.; Muhlemeier, J.; Trenkle, B. J. Organomet. Chem. 1985, **289**, 257.

144. Dotz, K. H.; Trenkle, B.; Schubert, U. Angew. Chem., Int. Ed. Engl. 1981, **20**, 287.

145. Grzegorzewska, U.; Leplawy, M.; Redlinski, A. Rocz. Chem. 1975, 1859 [C.A. 1976, **84**, 135059f].

146. Knunyants, I. L.; Cheburkov, Y. A. Izv. Akad. Nauk SSSR, Ser. Khim 1960, 678 [C.A. 1960, **54**, 22349c].

147. Zaitseva, G. S.; Vasil'eva, L. I.; Vinokurova, N. G.; Safronova, O. A.; Baukov, Y. I. Zh. Obshch. Khim. 1978, **48**, 1363 [C.A. 1978, **89**, 146998r].

148. England, D. C.; Krespan, C. G. J. Am. Chem. Soc. 1965, **87**, 4019.

149. Nations, R. G.; Hasek, R. H. U.S. Patent 3,221,028 [C.A. 1966, **64**, 4950e].

150. Brady, W. T.; Smith, L. Tetrahedron Lett. 1970, 2963.

151. Brady, W. T.; Patel, A. D. J. Heterocycl. Chem. 1971, **8**, 739.

152. Staudinger, H.; Bereza, S. Justus Liebigs Ann. Chem. 1911, **380**, 243.

153. Ogino, K.; Matsumoto, T.; Kozuka, S. J. Chem. Soc., Chem. Commun. 1979, 643.

154. Burpitt, R. D.; Brannock, K. C.; Nations, R. G.; Martin, J. C. J. Org. Chem. 1971, **36**, 2222.

155. Arjona, O.; de la Pradilla, R.; Perez, S.; Plumet, J.; Carrupt, P.; Vogel, P. Tetrahedron Lett. 1986, **27**, 5505.

156. Metzger, C.; Borrmann, D.; Wegler, R. Chem. Ber. 1967, **100**, 1817.

157. Turro, N. J.; Edelson, S.; Gagosian, R. J. Org. Chem. 1970, **35**, 2058.

158. Noels, A. F.; Herman, J. J.; Tyssie, P. J. Org. Chem. 1976, **41**, 2527.

159. Sheehan, J. J.; Buhle, E. L.; Corey, E. J.; Laubach, G. D.; Ryan, J. J. J. Am. Chem. Soc. 1950, **72**, 3828.

160. Williams, P. H.; Payne, G. B.; Sullivan, W. J.; Van Ess, P. R. J. Am. Chem. Soc. 1960, **82**, 4883.

161. Krabbenhoft, H. O. J. Org. Chem. 1978, **43**, 1305.

162. Pond, D. A. U.S. Patent 3,862,988, 1975 [C.A. 1976, **84**, 43304d].

163. Jowitt, H. Brit. Patent UK 885,217, 1961 [C.A. 1962, **57**, 4550a].

164. Probst, O.; Fernholz, H.; Mundlos, E.; Oheme, H.; Orth, A. U.S. Patent 3,113,149, 1963.

165. Chitwood, J. L.; Gott, P. G.; Krutak, J. J.; Martin, J. C. J. Org. Chem. 1971, **36**, 2216.

166. Brady, W. T.; Smith, L. J. Org. Chem. 1971, **36**, 1637.
167. Zaitseva, G. S.; Vinokurova, N. G.; Baukov, Y. I. Zh. Obshch. Khim. 1975, **45**, 1398 [C.A. 1975, **83**, 114548d].
168. Borrmann, D.; Wegler, R. Chem. Ber. 1966, **99**, 1245.
169. Borrmann, D.; Wegler, R. Chem. Ber. 1967, **100**, 1575.
170. Wynberg, H.; Staring, E. J. J. Am. Chem. Soc. 1982, **104**, 166.
171. Wynberg, H.; Staring, E. J. J. Org. Chem. 1985, **50**, 1977.
172. Staring, E. J.; Moorlag, H.; Wynberg, H. Recl. Trav. Chim. Pays-Bas 1986, **105**, 374.
173. Ketelaar, P. F.; Staring, E. J.; Wynberg, H. Tetrahedron Lett. 1985, **26**, 4665.
174. Wynberg, H.; Staring, E. G. J. PCT Int. Appl WO 84 01,577, 1984 [C.A. 1984, **101**, 230848r].
175. Lavallee, C.; Lemay, G.; Leborgne, A.; Spassky, N.; Prudhomme, R. Macromolecules 1984, **17**, 2457.
176. Voyer, R.; Prudhomme, R. J. Poly, Sci.: Part A: Polym. Chem. Ed. 1986, **24**, 2773.
177. Coyle, J. D.; Rapley, P. A.; Kamphuis, J.; Bos, H. J. J. Chem. Soc., Perkin Trans. 1 1985, 1957.
178. Kohn, H.; Charumilind, P.; Gopichand, Y. J. Org. Chem. 1978, **43**, 4961.
179. Drozd, V. N.; Popova, O. A. Zh. Obshch. Khim. 1979, **15**, 2602 [C.A. 1980, **92**, 163777x].
180. Takasu, I.; Higuchi, M.; Suzuki, R. Jpn. Kokai JP 73 12,736.
181. Vanderkooi, N.; Huthwaite, H. J. U.S. Patent 3,894,097, 1975 [C.A. 1975, **83**, 148015t].
182. Moore, H. W.; Mercer, F.; Kunert, D.; Albaugh, P. J. Am. Chem. Soc. 1979, **101**, 5435.
183. Morita, N.; Asao, T.; Ojima, J.; Wada, K. Chem. Lett. 1981, 57.
184. Neidlein, R.; Humburg, G. Justus Liebigs Ann. Chem. 1978, 1974.
185. Brady, W. T.; Giang, Y. F., Marchand, A. P.; Wu, A. J. Org. Chem. 1987, **52**, 3457.
186. Rioult, P.; Vialle, J. Bull., Soc. Chim. Fr. 1967, 2883.
187. Asao, T. Synth. Commun. 1972, **2**, 353.
188. Martin, J. C.; Burpitt, R. D.; Gott, P. G.; Harris, M.; Meen, R. H. J. Org. Chem. 1971, **36**, 2205.
189. Farbwerke Hoechst, British UK Pat. GB 939,844, 1963.
190. Mundlos, E.; Graf, R. Justus Liebigs Ann. Chem. 1964, **677**, 108.
191. Goldish, D. M.; Axon, B. W.; Moore, H. W. Heterocycles 1983, **20**, 187.
192. Brady, W. T.; Schieh, C. H. J. Heterocycl. Chem. 1985, **22**, 357.

193. Schaumann, E.; Behr, H.; Adiwidjaja, G. Justus Liebigs Ann. Chem. 1979, 1322.
194. Belzecki, C.; Krawczyk, Z. J. Chem. Soc., Chem. Commun. 1977, 302.
195. Jäger, U.; Schwab, M.; Sundermeyer, W. Chem. Ber. 1986, **119**, 1127.
196. Beecken, H.; Korte, F. Tetrahedron 1962, **18**, 1527.
197. Semple, J. E.; Joullie, M. M. J. Org. Chem. 1978, **43**, 3066.
198. Neidlein, R.; Lehr, W. Heterocycles 1981, **16**, 1187.
199. Kerber, R. C.; Cann, M. C. J. Org. Chem. 1974, **39**, 2552.
200. Kresze, G.; Trede, A. Tetrahedron 1963, **19**, 133.
201. Hall, J. H.; Kellogg, R. M. J. Org. Chem. 31, **1966**, 1079.
202. Ried, W.; Piesch, S. Chem. Ber. 1966, **99**, 233.
203. Fahr, E.; Fischer, W.; Jung, A.; Sauer, L. Tetrahedron Lett. 1967, 161.
204. Ingold, C. K.; Weaver, S. D. J. Chem. Soc. 1925, **127**, 378.
205. Sommer, S. Angew. Chem. 1976, **88**, 449.
206. Ried, W.; Dietrich, R. Justus Liebigs Ann. Chem. 1963, **666**, 113.
207. Staudinger, H. Ber. 1911, **44**, 1619.
208. Texier, F.; Carrié, R.; Jaz, J. J. Chem. Soc., Chem. Commun. 1972, 199.
209. Abou-Gharbia, M. A.; Joullie, M. M. Heterocycles 1978, **9**, 457.
210. Singal, K. K. Chem. Ind. (London) 1985, 761.
211. Scarpati, R.; Sorrentino, P. Gazz. Chim. Ital. 1959, **89**, 1525 [C.A. 1960, **54**, 22570d].
212. Evans, A. R.; Taylor, G. A. J. Chem. Soc., Perkin Trans. 1 1983, 979.
213. Alsop, S. H.; Barr, J. J.; Storr, R. C.; Cameron, A. F.; Freer, A. A. J. Chem. Soc., Chem. Commun. 1976, 888.
214. van Tilborg, W. J. M.; Steinberg, H.; de Boer, T. J. Synth. Commun. 1973, **3**, 189.
215. Rothgery, E. F.; Holt, R. J.; McGee, H. A. J. Am. Chem. Soc. 1975, **97**, 4971.
216. Turro, N. J.; Hammond, W. B. J. Am. Chem. Soc. 1966, **88**, 3672.
217. Schaafsma, S. E.; Steinberg, H.; De Boer, T. J. Recl. Trav. Chim. Pays-Bas 1966, **85**, 1170.
218. Hammond, W. B.; Turro, N. J. J. Am. Chem. Soc. 1966, **88**, 2880.
219. Saitseva, G. S.; Bogdanova, G. S.; Baukov, Y. I.; Lutsenko, I. F. Zh. Obshch. Khim. 1978, **48**, 131 [C.A. 1978, **88**, 170250r].
220. Zaitseva, G. S.; Bogdanova, G. S.; Baukov, Y. I.; Lutsenko, I. F. J. Organomet. Chem. 1976, **121**, C21.
221. Ter-Gabrielyan, E. G.; Avetisyan, E. A.; Gambaryan, N. P. Izv. Akad. Nauk SSSR, Ser. Khim. 1973, 2562 [C.A. 1974, **80**, 59886y].

222. Ried, W.; Kraemer, R. Justus Liebigs Ann. Chem. 1973, 1952.
223. Yates, P.; Clark, T. J. Tetrahedron Lett. 1961, 435.
224. Toppet, S.; L'abbé, G.; Smets, G. Chem. Ind. (London) 1973, 1110.
225. Ikeda, K.; L'abbé, G.; Smets, G. Chem. Ind. (London) 1973, 327.
226. Tsuge, O.; Urano, S.; Oe, K. J. Org. Chem. 1980, **45**, 5130.
227. Moriarty, R. M.; White, K. B.; Chin, A. J. Am. Chem. Soc. 1978, **100**, 5582.
228. Hatakeyama, S.; Honda, S.; Akimoto, H. Bull. Chem. Soc. Jpn. 1985, **58**, 2411.
229. Wheland, R.; Bartlett, P. D. J. Am. Chem. Soc. 1970, **92**, 6057.
230. Dennis, N.; Katritzky, A. R.; Sabounji, G. J. Tetrahedron Lett. 1976, 2959.
231. Cheburkov, Y. A.; Mukhamadaliev, N.; Knunyants, I. L. Tetrahedron 1968, **24**, 1341.
232. Cheburkov, Y. A.; Mukhamadaliev, N.; Knunyants, I. L. Izv. Akad. Nauk SSSR, Ser. Khim. 1966, 383 [C.A. 1966, **64**, 17411d].
233. Falshaw, C.; Lakoues, A.; Taylor, G. J. Chem. Res. (S) 1985, 106.
234. Mayr, H.; Heigl, U. W. J. Chem. Soc., Chem. Commun. 1987, 1804.
235. Brady, W. T.; Agho, M. O. J. Heterocycl. Chem. 1983, **20**, 501.
236. Katritzky, A. R.; Cutler, A. T.; Dennis, N.; Sabongi, G. J.; Rahimi-Rastgoo, S.; Fischer, G. W.; Fletcher, I. J. J. Chem. Soc., Perkin Trans. 1 1980, 1176.
237. Gouesnard, J. P. Tetrahedron 1974, **30**, 3117.
238. Brady, W. T.; Agho, M. O. Synthesis 1982, 500.
239. Jaworski, T.; Kwiatkowski, S. Roczniki Chemii 1975, **49**, 63 [C.A. 1975, **83**, 58593a].
240. Tanimoto, S.; Matsumura, Y.; Sugimoto, T.; Okano, M. Tetrahedron Lett. 1977, 2899.
241. Krishan, K.; Singh, A.; Singh, B.; Kumar, S. Synth. Commun. 1984, **14**, 219.
242. Duran, F.; Ghosez, L. Tetrahedron Lett. 1970, 245.
243. Sakamoto, M.; Miyazawa, K.; Kuwabara, K.; Tomimatsu, Y. Heterocycles 1979, **12**, 231.
244. Fitton, A. O.; Frost, J. R.; Houghton, P. G.; Suschitzky, H. J. Chem. Soc., Perkin Trans. 1 1977, 1450.
245. Luthardt, P.; Würthwein, E. Tetrahedron Lett. 1988, **29**, 921.
246. Katagiri, N.; Kato, T.; Niwa, R. J. Heterocycl. Chem. 1984, **21**, 407.
247. Satsumabayashi, S.; Motoki, S.; Nakano, H. J. Org. Chem. 1976, **41**, 156.

248. Sakamoto, M.; Miyazawa, K.; Tomimatsu, Y. Chem. Pharm. Bull. 1976, **24**, 2532.
249. Goerdeler, J.; Lohmann, H. Chem. Ber. 1977, **110**, 2996.
250. Ried, W.; Radt, W. Justus Liebigs Ann. Chem. 1965, **688**, 170.
251. Friedrichsen, W.; Oeser, H. Chem. Ber. 1975, **108**, 31.
252. Staudinger, H.; Endle, R. Justus Liebigs Ann. Chem. 1913, **401**, 263.
253. Campbell, N.; Davison, P. S.; Heller, H. G. J. Chem. Soc. 1963, 993.
254. Campbell, N.; Davison, P. S. Chem. Ind. (London) 1962, 2012.
255. Mosti, L.; Menozzi, G.; Bignardi, G.; Schenone, P. Il Farmaco (Ed. Sci.) 1977, **32**, 794 [C.A. 1978, **88**, 62262n].
256. Eiden, F.; Breugst, I. Chem. Ber. 1979, **112**, 1791.
257. Rokhlin, E. M.; Gambaryan, N. P.; Knunyants, I. L. Izv. Akad. Nauk SSSR, Ser. Khim. 1963, 1952 [C.A. 1964, **60**, 7454a].
258. Mosti, L.; Schenone, P.; Menozzi, G. J. Heterocycl. Chem. 1978, **15**, 181.
259. Opitz, G.; Zimmerman, F. Chem. Ber. 1964, **97**, 1266.
260. Meslin, J. C.; N'Guessan, Y. T.; Quiniou, H.; Tonnard, F. Tetrahedron 1975, **31**, 2679.
261. Meslin, J. C.; Quiniou, H. Bull. Soc. Chim. Fr. 1972, 2517.
262. Bachi, M. D.; Rothfield, M. J. Chem. Soc., Perkin Trans. 1 1972, 2326.
263. Goerdeler, J.; Schimpf, R.; Tiedt, M. Chem. Ber. 1972, **105**, 3322.
264. Goerdeler, J.; Hohage, H. Chem. Ber. 1973, **106**, 1487.
265. Katrizky, A. R.; Cutler, A. T.; Dennis, N.; Rahimi-Rastgoo, S.; Sabongi, G. J. Z. Chem. 1979, **19**, 20.
266. Kniezo, L.; Kristian, P., Imrich, J.; Ugozzoli, F.; Andreetti, G. Tetrahedron 1988, **44**, 543.
267. Fahr, E. Angew. Chem. 1964, **76**, 505.
268. Sommer, S. Angew. Chem. 1977, **89**, 59.
269. Meslin, J. C.; Quiniou, H. Synthesis 1974, 298.
270. Ooka, M.; Kitamura, A.; Okazaki, R.; Inamoto, N. Bull. Chem. Soc. Jpn. 1978, **51**, 301.
271. Okazaki, R.; Ooka, M.; Inamoto, N. J. Chem. Soc., Chem. Commun. 1976, 562.
272. Gotthardt, H.; Schenk, K. Angew. Chem. 1985, **97**, 604.
273. Danheiser, R. L.; Sard, H. J. Org. Chem. 1980, **45**, 4810.
274. Jäger, G.; Wenzelburger, J. Justus Liebigs Ann. Chem. 1976, 1689.
275. Hünig, S.; Benzing, E.; Hubner, K. Chem. Ber. 1961, **94**, 486.
276. Berge, J. M.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1982, **65**, 2230.

277. Crabtree, H. E.; Smalley, R. K.; Suschitzky, H. J. Chem. Soc. (C) 1968, 2730.
278. Ficini, J.; Pouliquen, J. Tetrahedron Lett. 1972, 1135.
279. Himbert, G.; Henn, L. Justus Liebigs Ann. Chem. 1987, 381.
280. Jäger, G. Chem. Ber. 1972, **105**, 137.
281. Stetter, H.; Kiehs, K. Chem. Ber. 1965, **98**, 2099.
282. Hyatt, J. A.; Feldman, P. L.; Clemens, R. J. J. Org. Chem. 1984, **49**, 5105.
283. Ziegler, E.; Kleineberg, G.; Meindl, H. Monatsh. Chem. 1966, **97**, 10.
284. Selvarajan, R.; Narasimhan, K.; Swaminathan, S. Tetrahedron Lett. 1967, 2089.
285. Goerdeler, J.; Köhler, H. Tetrahedron Lett. 1976, 2961.
286. Capuano, L.; Urhahn, G.; Willmes, A. Chem. Ber. 1979, **112**, 1012.
287. Minami, T.; Yamauchi, Y.; Ohshiro, Y.; Murai, S.; Sonoda, N. J. Chem. Soc., Perkin Trans. 1 1977, 904.
288. Day, A. C.; McDonald, A. N.; Anderson, B. F.; Bartczak, T. J.; Hodder, O. J. J. Chem. Soc., Chem. Commun. 1973, 247.
289. Rees, C. W.; Somanathan, R.; Storr, R. C.; Woolhouse, A. D. J. Chem. Soc., Chem. Commun. 1976, 125.
290. Stetter, H.; Kiehs, K. Chem. Ber. 1965, **98**, 2099.
291. Capuano, L.; Gärtner, K. J. Heterocycl. Chem. 1981, **18**, 1341.
292. Turro, N. J.; Chow, M.-F.; Ito, Y. J. Am. Chem. Soc. 1978, **100**, 5580.
293. Bestian, H.; Günther, D. Angew. Chem. Int. Ed. Engl. 1963, **2**, 608.
294. Frey, H. M.; Isaacs, N. S. J. Chem. Soc. (B) 1970, 830.
295. Bartlett, P. D.; McCluney, R. E. J. Org. Chem. 1983, **48**, 4165.
296. Williams, J. W.; Hurd, C. D. J. Org. Chem. 1940, **5**, 122.
297. Smith, C. W.; Norton, D. G. *Org. Synth. Coll. Vol. IV*, 348, 1963, Wiley, New York, 1963.
298. Krepski, L. R.; Hassner, A. J. Org. Chem. 1978, **43**, 2879.
299. Johnston, B. D.; Czyzewska, E.; Oehlschlager, A. C. J. Org. Chem. 1987, **52**, 3693.
300. Weyler, W.; Duncan, W. G.; Liewen, M. B.; Moore, H. W. Org. Synth. 1976, **55**, 32.
301. Weyler, W.; Duncan, W. G.; Liewen, M. B.; Moore, H. W. *Org. Synth. Coll. Vol. VII*, 210, Wiley, New York, 1990.
302. Arya, F.; Bouquant, J.; Chuche, J. Tetrahedron Lett. 1986, **27**, 1913.
303. Huber, U. A.; Dreiding, A. S. Helv. Chim. Acta 1970, **53**, 495.
304. Baxter, G. J.; Brown, R. F. C.; Eastwood, F. W.; Harrington, K. J. Tetrahedron Lett. 1975, 4283.

305. Danheiser, R. L.; Gee, S. K.; Sard, H. J. Am. Chem. Soc. 1982, **104**, 7670.
306. Hassner, A.; Naidorf, S. Tetrahedron Lett. 1986, **27**, 6389.
307. Wright, B. B. J. Am. Chem. Soc. 1988, **110**, 4456.
308. Ainsworth, C.; Chen, F.; Kuo, Y. J. Organomet. Chem. 1972, **46**, 59.
309. Ripoll, J. L. Tetrahedron 1977, **33**, 389.
310. Kunert, D. M.; Chambers, R.; Mercer, F.; Hernandez, L.; Moore, H. W. Tetrahedron Lett. 1978, 929.
311. Moore, H. W.; Hernandez, L.; Sing, A. J. Am. Chem. Soc. 1976, **98**, 3728.
312. Fishbein, P. L.; Moore, H. W. J. Org. Chem. 1984, **49**, 2190.
313. Yates, P.; Crawford, R. J. J. Am. Chem. Soc. 1966, **88**, 1562.
314. Horner, L.; Spietschka, E.; Gross, A. Justus Liebigs Ann. Chem. 1951, **573**, 17.
315. Becker, D.; Birnbaum, D. J. Org. Chem. 1980, **45**, 578.
316. Ciabattoni, J.; Anderson, H. Tetrahedron Lett. 1967, 3377.
317. Greene, A. E.; Lansard, J. P.; Luche, J. L.; Petrier, C. J. Org. Chem. 1984, **49**, 931.
318. Grieco, P. A. J. Org. Chem. 1972, **37**, 2363.
319. Nee, M.; Roberts, J. D. J. Org. Chem. 1981, **46**, 67.
320. Hasek, R. H.; Elam, E. U. Canadian Patent CA 618,772, 1962.
321. Hasek, R. H.; Gott, P. G.; Martin, J. C. J. Org. Chem. 1964, **29**, 1239.
322. Brady, W. T.; Marchand, A. P.; Giang, Y. F.; Wu, A. Synthesis 1987, 395.
323. Hyatt, J. A. U.S. Patent 4,621,146 [C.A. 1987, **106**, 119677y].
324. Borrmann, D.; Wegler, R. Chem. Ber. 1969, **102**, 64.
325. Neidlein, R.; Cepera, K. Chem. Ber. 1978, **111**, 1824.
326. Kellogg, R. M. J. Org. Chem. 1973, **38**, 844.
327. Brady, W. T.; Agho, M. O. J. Org. Chem. 1983, **48**, 5337.
328. Brady, W. T.; Hoff, E. F., Jr. J. Am. Chem. Soc. 1968, **90**, 6256.
329. Grimme, W.; Schneider, E. Angew. Chem. 1977, **89**, 754.
330. Krügerke, T.; Buschmann, J.; Kleemann, G.; Luger, P.; Seppelt, K. Angew. Chem. Int. Ed. Engl. 1987, **26**, 799.
331. Sauer, J. C. J. Am. Chem. Soc. 1947, **69**, 2444.
332. Reid, E. B.; Groszos, S. J. J. Am. Chem. Soc. 1953, **75**, 1655.
333. Staudinger, H. Ber. 1911, **44**, 533.
334. McCarney, C. C.; Ward, R. S. J. Chem. Soc., Perkin Trans. 1 1975, 1600.

335. Enk, E.; Spes, H. Angew. Chem. 1961, **73**, 334.
336. England, D. C.; Krespan, C. G. J. Org. Chem. 1970, **35**, 3322.
337. Trahanovsky, W. S.; Serber, B. W.; Wilkes, M. C.; Preckel, M. M. J. Am. Chem. Soc. 1982, **104**, 6779.
338. Wear, R. L. J. Am. Chem. Soc. 1951, **73**, 2390.
339. Wedekind, E.; Weisswange, W. Ber. 1906, **39**, 1631.
340. Staudinger, H. Justus Liebigs Ann. Chem. 1907, **356**, 51.
341. Staudinger, H.; Schneider, H.; Schotz, P.; Strong, P. M. Helv. Chim. Acta 1923, **6**, 291.
342. Elam, E. U. J. Org. Chem. 1967, **32**, 215.
343. Payne, G. B. J. Org. Chem. 1966, **31**, 718.
344. Berkowitz, W. F.; Ozorio, A. A. J. Org. Chem. 1975, **40**, 527.
345. Erickson, J. L. E.; Collins, F. E.; Owen, B. L. J. Org. Chem. 1966, **31**, 480.
346. England, D. C. J. Org. Chem. 1981, **46**, 147.
347. Brady, W. T.; Ting, P. L. J. Org. Chem. 1976, **41**, 2336.
348. Staudinger, H.; Maier, J. Justus Liebigs Ann. Chem. 1913, **401**, 292.
349. Baldwin, J. E. J. Org. Chem. 1963, **28**, 3112.
350. Berkowitz, W. F.; Ozorio, A. A. J. Org. Chem. 1971, **36**, 3787.
351. Hoffmann, H. M. R.; Wulff, J. M.; Kütz, A.; Wartchow, R. Angew. Chem. Suppl. 1982, 17.
352. Brady, W. T.; Cheng, T. C. J. Org. Chem. 1977, **42**, 732.
353. Moore, H. W.; Weyler, W. J. Am. Chem. Soc. 1970, **92**, 4132.
354. Walborsky, H. M.; Buchman, E. R. J. Am. Chem. Soc. 1953, **75**, 6339.
355. Hill, C. M.; Senter, G. W. J. Am. Chem. Soc. 1949, **71**, 364.
356. Farnum, D. G.; Webster, B. J. Am. Chem. Soc. 1963, **85**, 3502.
357. Baldwin, J. E.; Roberts, J. D. J. Am. Chem. Soc. 1963, **84**, 2444.
358. Franke, W. K. R.; Ahne, H. Angew. Makromol. Chem. 1972, **21**, 195.
359. Mormann, W.; Hoffmann, S.; Hoffmann, W. Chem. Ber. 1987, **120**, 285.
360. Buchta E.; Geibel, K. Justus Liebigs Ann. Chem. 1964, **678**, 53.
361. Baldwin, J. E. J. Org. Chem. 1964, **29**, 1882.
362. Buchta, E.; Fischer, M. Ber. 1966, **99**, 1509.
363. Dehmlow, E. V.; Slopianka, M.; Pickardt, J. Justus Liebigs Ann. Chem. 1979, 572.
364. Farnum, D. G.; Webster, B.; Wolf, A. D. Tetrahedron Lett. 1968, 5003.
365. Buchta, E.; Theuer, W. Justus Liebigs Ann. Chem. 1963, **666**, 81.
366. Bamberger, E.; Baum, M.; Schlein, L. J. Prakt. Chem. 1921, **105**, 266.
367. Karmarkar, S. S.; Sharma, M. M. Indian J. Chem., Sect. A 1970, **8**, 413

[C.A. 1970, **73**, 35148p].

368. Buchta, E.; Merk, W. Justus Liebigs Ann. Chem. 1966, **694**, 1.
369. Corbellini, A.; Maggioni, P.; Pietta, P. G. Gazz. Chim. Ital. 1967, **97**, 1126 [C.A. 1968, **68**, 50047v].
370. Strating, J.; Scharp, J.; Wynberg, H. Recl. Trav. Chim. Pays-Bas 1970, **89**, 23.
371. Baldwin, J. E. J. Org. Chem. 1964, **29**, 1880.
372. Staudinger, H.; Suter, E. Ber. 1912, **53**, 1092.
373. Erickson, J. L. E.; Kitchens, G. C. J. Org. Chem. 1962, **27**, 460.
374. Kimbrough, R. D., Jr. J. Org. Chem. 1964, **29**, 1246.
375. Anet, R. Chem. Ind. (London) 1961, 1313.
376. Dehmlow, S. S.; Dehmlow, E. V. Justus Liebigs Ann. Chem. 1975, 209.
377. Wentrup, C.; Winter, H.; Gross, G.; Netsch, K.; Kollenz, G.; Ott, W.; Biedermann, A. Angew. Chem., Int. Ed. Engl. 1984, **23**, 800.
378. Leuchs, H.; Wutke, J.; Gieseler, E. Ber. 1913, **46**, 2200.
379. Rothman, E. S. J. Org. Chem. 1967, **32**, 1683.
380. Chickos, J. S.; Sherwood, D. E.; Jug, K. J. Org. Chem. 1978, **43**, 1146.
381. Birum, G. H.; Matthews, C. N. J. Am. Chem. Soc. 1968, **90**, 3842.
382. Roberts, J. D.; Armstrong, R.; Trimble, R. F.; Burg, M. J. Am. Chem. Soc. 1949, **71**, 843.
383. Brady, W. T.; Ting, P. L. Tetrahedron Lett. 1974, 2619.
384. Livantsova, L. I.; Zaitseva, G. S.; Bekker, R. A.; Baukov, Y. A.; Lutsenko, I. F. Zh. Obshch. Khim. 1980, **50**, 475. [C.A. 1980, **92**, 215485x].
385. Stetter, H.; Kiehs, K. Tetrahedron Lett. 1964, 3531.
386. Huisgen, R.; Feiler, L. A. Chem. Ber. 1969, **102**, 3391.
387. Cheburkov, Y. A.; Mukhamadaliev, N.; Knunyants, I. L. Bull. Acad. Sci USSR, Div. Chem. Sci. 1966, 362 [C.A. 1966, **64**, 17438a].
388. Martin, P.; Greuter, H.; Bell °s, D. J. Am. Chem. Soc. 1979, **101**, 5853.
389. Bell °s, D. Pure Appl. Chem. 1985, **57**, 1827.
390. Huisgen, R.; Mayr, H. Tetrahedron Lett. 1975, 2969.
391. DoMinh, T.; Strausz, O. P. J. Am. Chem. Soc. 1970, **92**, 1766.
392. Brook, P. R.; Hunt, K. J. Chem. Soc., Chem. Commun. 1974, 989.
393. Brady, W. T.; Hieble, J. P. J. Org. Chem. 1971, **36**, 2033.
394. Neidlein, R.; Bernhard, E. Angew. Chem., Int. Ed. Engl. 1978, **17**, 369.
395. Binsch, G.; Feiler, L. A.; Huisgen, R. Tetrahedron Lett. 1968, 4497.
396. Farooq, M. O.; Vahidy, T. A.; Husain, S. M. Bull. Soc. Chim. Fr. 1958, 830.
397. Erden, I.; Sorenson, E. M. Tetrahedron Lett. 1983, **24**, 2731.

398. Brook, P. R.; Griffiths, J. G. J. Chem. Soc., Chem. Commun. 1970, 1344.

399. Brady, W. T.; Patel, A. D. J. Org. Chem. 1973, **38**, 4106.

400. Bak, D. A.; Brady, W. T. J. Org. Chem. 1979, **44**, 107.

401. Brook, P. R.; Eldeeb, A. M.; Hunt, K.; McDonald, W. S. J. Chem. Soc., Chem. Commun. 1978, 10.

402. Nguyen, N. V.; Chow, K.; Moore, H. W. J. Org. Chem. 1987, **52**, 1315.

403. Brady, W. T.; Waters, O. H. J. Org. Chem. 1967, **32**, 3703.

404. Malherbe, R.; Rist, G.; Belluš, D. J. Org. Chem. 1983, **48**, 860.

405. Hasek, R. H.; Gott, P. G.; Martin, J. C. J. Org. Chem. 1966, **31**, 1931.

406. de Meijere, A.; Erden, I.; Weber, W.; Kaufmann, D. J. Org. Chem. 1988, **53**, 152.

407. Weber, W.; Erden, I.; de Meijere, A. Angew. Chem. 1980, **92**, 387.

408. Maurin, R.; Bertrand, M. Bull. Soc. Chim. Fr. 1970, 998.

409. Jackson, D. A.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1983, **66**, 2330.

410. van der Bij, J. R.; Kooyman, E. C. Recl. Trav. Chim. Pays-Bas 1952, **71**, 837.

411. Danheiser, R. L.; Martinez-Davila, C.; Sard, H. Tetrahedron 1981, **37**, 3943.

412. Farmer, E. H.; Farooq, M. O. Chem. Ind. (London) 1937, 1079.

413. Fitjer, L.; Kanschik, A.; Majewski, M. Tetrahedron Lett. 1988, **29**, 5525.

414. Dunkelblum, E. Tetrahedron 1976, **32**, 975.

415. Wiseman, J. R.; Chan, H. F. J. Am. Chem. Soc. 1970, **92**, 4749.

416. Hassner, A.; Pinnick, H. W.; Ansell, J. M. J. Org. Chem. 1978, **43**, 1774.

417. Aljancic-Solaja, I.; Rey, M.; Dreiding, A. S. Helv. Chim. Acta 1987, **70**, 1302.

418. Becherer, J.; Hauel, N.; Hoffmann, R. W. Justus Liebigs Ann. Chem. 1978, 312.

419. Donskaya, N. A.; Bessmertnykh, A. G.; Drobysh, V. A.; Shabarov, Y. S. Zh. Org. Khim. 1987, **23**, 745 [C.A. 1988, **108**, 74844y].

420. Fitjer, L.; Kanschik, A.; Majewski, M. Tetrahedron Lett. 1985, **26**, 5277.

421. Fitjer, L.; Quabeck, U. Angew. Chem., Int. Ed. Engl. 1987, **26**, 1023.

422. Wiel, J.; Rouessac, F. Bull. Soc. Chim. Fr. 1979, II-273.

423. Senft, E.; Maurin, R. C. R. Acad. Sci. Paris, Série C 1972, **275**, 1113.

424. Mehta, G.; Rao, H. S. P. Synth. Commun. 1985, **15**, 991.

425. Trah, S.; Weidmann, K.; Fritz, H.; Prinzbach, H. Tetrahedron Lett. 1987, **28**, 4399.

426. Sasaki, T.; Hayakawa, K.; Manabe, T.; Nishida, S. J. Am. Chem. Soc.

1981, **103**, 565.

427. Yang, C. H.; Lin H. C.; Whang, M. J. J. Chin. Chem. Soc. (Taipei) 1986, **33**, 139.
428. Terlinden, R.; Boland, W.; Jaenicke, L. Helv. Chim. Acta 1983, **66**, 466.
429. Aue, D. H.; Shellhamer, D. F.; Helwig, G. S. J. Chem. Soc., Chem. Commun. 1975, 603.
430. Harding, K. E.; Trotter, J. W.; May, L. Synth. Commun. 1972, **2**, 231.
431. Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. Tetrahedron 1971, **27**, 615.
432. Ali, S. M.; Roberts, S. M. J. Chem. Soc., Chem. Commun. 1975, 887.
433. Hassner, A.; Dillon, J.; Onan, K. D. J. Org. Chem. 1986, **51**, 3315.
434. Smith, L. R.; Gream, G. E.; Meinwald, J. J. Org. Chem. 1977, **42**, 927.
435. Gream, G. E.; Smith L. R.; Meinwald, J. J. Org. Chem. 1974, **39**, 3461.
436. Wiberg, K. B.; Jason, M. E. J. Am. Chem. Soc. 1976, **98**, 3393.
437. Aue, D. H.; Helwig, G. S. J. Chem. Soc., Chem. Commun. 1974, 925.
438. Witzeman, J. S.; Ph.D. Dissertation, University of California, Santa Barbara, 1984.
439. Jeffs, P. W.; Molina, G.; Cass, M. W.; Cortese, N. A. J. Org. Chem. 1982, **47**, 3871.
440. Jeffs, P. W.; Molina, G. J. Chem. Soc., Chem. Commun. 1973, 3.
441. Ghosez, L.; Montaigne, R.; Vanlierde, H.; Dumay, F. Angew. Chem., Int. Ed. Engl. 1968, **7**, 643.
442. Brady, W. T.; Roe, R. J. Am. Chem. Soc. 1971, **93**, 1662.
443. Dehmlow, E. V.; Birkhahn, M. Justus Liebigs Ann. Chem. 1987, 701.
444. Staudinger, H.; Suter, E. Ber. 1912, **53**, 1092.
445. Smith, L. I.; Agre, C. L.; Leekley, R. M.; Prichard, W. W. J. Am. Chem. Soc. 1939, **61**, 7.
446. DeSelms R. C.; Delay, F. J. Org. Chem. 1972, **37**, 2908.
447. Gheorghiu, M. D.; Filip, P.; Drăghici, C.; Pârvulescu, L. J. Chem. Soc., Chem. Commun. 1975, 635.
448. Feiler, L. A.; Huisgen, R.; Koppitz, P. J. Am. Chem. Soc. 1974, **96**, 2270.
449. Lange, G.; Savard, M. E.; Viswanatha, T.; Dmitrienko, G. I. Tetrahedron Lett. 1985, **26**, 1791.
450. Hassner, A.; Cory, R. M.; Sartoris, N. J. Am. Chem. Soc. 1976, **98**, 7698.
451. Cory, R. M.; Hassner, A. Tetrahedron Lett. 1972, 1245.
452. Greene, A. E. Tetrahedron Lett. 1980, **21**, 3059.
453. Mehta, G.; Rao, K. S. Tetrahedron Lett. 1984, **25**, 1839.
454. Jendralla, H. Tetrahedron 1983, **39**, 1359.

455. Erden, I. Tetrahedron Lett. 1984, **25**, 1535.
456. Mehta, G.; Padma, S.; Rao, K. S. Synth. Commun. 1985, **15**, 1137.
457. Krapcho, A. P.; Lesser, J. H. J. Org. Chem. 1966, **31**, 2030.
458. Ziegler, K.; Sauer, H.; Bruns, L.; Froitzheim-Kühlhorn, H.; Schneider, J. Justus Liebigs Ann. Chem. 1954, **589**, 122.
459. Skattebøl, L.; Stenstrøm, Y. Acta Chem. Scand., Ser. B 1985, **39**, 291.
460. Hoch, H.; Hünig, S. Chem. Ber. 1972, **105**, 2660.
461. Greene, A. E.; Coelho, F.; Deprés, J. P.; Brocksom, T. J. Tetrahedron Lett. 1988, **29**, 5661.
462. Johnston, B. D.; Slessor, K. N.; Oehlschlager, A. C. J. Org. Chem. 1985, **50**, 114.
463. Turner, R. W.; Seden, T. J. Chem. Soc., Chem. Commun. 1966, 399.
464. Asao, T.; Morita, N.; Kitahara, Y. J. Am. Chem. Soc. 1972, **94**, 3655.
465. Campbell, N.; Heller, H. G. J. Chem. Soc. 1965, 5473.
466. Becker, K. B.; Hohermuth, M. K.; Rihs, G. Helv. Chim. Acta 1982, **65**, 235.
467. Wiel, J. B.; Rouessac, F. J. Chem. Soc., Chem. Commun. 1975, 180.
468. Stevens, H. C. US Patent 3,440,284 (1969) [C. A. 1969, **71**, 60866n].
469. Hassner, A.; Fletcher V. R.; Hamon, D. P. G. J. Am. Chem. Soc. 1971, **93**, 264.
470. Tsunetsugu, J.; Asai, M.; Hiruma, S.; Kurata, Y.; Mori, A.; Ono, K.; Uchiyama, H.; Sato, M.; Ebine, S. J. Chem. Soc., Perkin Trans. 1 1983, 285.
471. Oda, M.; Morita, N.; Asao, T. Chem. Lett. 1981, 1165.
472. Scott, L. T.; Erden, I.; Brunsvold, W. R.; Schultz, T. H.; Houk, K. N.; Paddon-Row, M. N. J. Am. Chem. Soc. 1982, **104**, 3659.
473. Mehta, G.; Nair, M. S. J. Chem. Soc., Chem. Commun. 1983, 439.
474. Mehta, G.; Nair, M. S. J. Am. Chem. Soc. 1985, **107**, 7519.
475. Ried, W.; Bellinger, O. Synthesis 1982, 729.
476. Rosini, G.; Ballini, R.; Zanotti, V. Tetrahedron 1983, **39**, 1085.
477. Inamoto, Y.; Fujikura, Y.; Ikeda, H.; Takaishi, N. Jpn. Kokai JP 77 10,252 [C. A. 1977, **87**, 52880c].
478. Inamoto, Y.; Fujikura, Y.; Ikeda, H.; Takaishi, N. Jpn. Kokai JP 77 10,249 [C. A. 1977, **87**, 52881d].
479. Greene, A. E.; Luche, M. J.; Deprés, J. P. J. Am. Chem. Soc. 1983, **105**, 2435.
480. Tsunetsugu, J.; Kanda, M.; Takahashi, M.; Yoshida, K.; Koyama, H.; Shiraishi, K.; Takano, Y.; Sato, M.; Ebine, S. J. Chem. Soc., Perkin Trans. 1 1984, 1465.

481. Tsunetsugu, J.; Sato, M.; Kanda, M.; Takahashi, M.; Ebine, S. Chem. Lett. 1977, 885.
482. Gleiter, R.; Dobler, W. Chem. Ber. 1985, **118**, 4725.
483. Kelly, R. C.; VanRheenen, V.; Schletter, I.; Pillai, M. D. J. Am. Chem. Soc. 1973, **95**, 2746.
484. Sugihara, Y.; Fujita, H.; Murata, I. J. Chem. Soc. Chem. Commun. 1986, 1130.
485. Jeffs, P. W.; Cortese, N. A.; Wolfram, J. J. Org. Chem. 1982, **47**, 3881.
486. Mehta, G.; Raja Reddy, K. Tetrahedron Lett. 1988, **29**, 3607.
487. Taylor, G. A.; Yildirir, S. J. Chem. Soc., Perkin Trans. 1 1981, 3129.
488. Wakamatsu, T.; Miyachi, N.; Ozaki, F.; Shibasaki, M.; Ban, Y. Tetrahedron Lett. 1988, **29**, 3829.
489. Cragg, G. M. L. J. Chem. Soc. (C) 1970, 1829.
490. Fletcher, V. R.; Hassner, A. Tetrahedron Lett. 1970, 1071.
491. Brady, W. T.; O'Neal, H. R. J. Org. Chem. 1967, **32**, 2704.
492. Chickos, J. S.; Frey, H. M. J. Chem. Soc., Perkin Trans. 2 1987, 365.
493. Martin, J. C.; Gott, P. G.; Goodlett, V. W.; Hasek, R. H. J. Org. Chem. 1965, **30**, 4175.
494. Huisgen, R.; Otto, P. Chem. Ber. 1969, **102**, 3475.
495. Gouesnard, J. P. Tetrahedron 1974, **30**, 3113.
496. Gouesnard, J. P. C. R. Acad. Sci. Paris, Série C 1973, **277**, 883.
497. Grimme, W.; Köser, H. G. Angew. Chem. 1980, **92**, 307.
498. Coates, R. M.; Robinson, W. H. J. Am. Chem. Soc. 1972, **94**, 5920.
499. Brady, W. T.; Lloyd, R. M. J. Org. Chem. 1981, **46**, 1322.
500. Kakiuchi, K.; Hiramatsu, Y.; Tobe, Y.; Odaira, Y. Bull. Chem. Soc. Jpn. 1980, **53**, 1779.
501. Sasaki, T.; Manabe, T.; Hayakawa, K. Tetrahedron Lett. 1981, **22**, 2579.
502. Harmon, R. E.; Barta, W. D.; Gupta, S. K.; Slomp, G. J. Chem. Soc. (C) 1971, 3645.
503. Harmon, R. E.; Barta, W. D.; Gupta, S. K.; Slomp, G. J. Chem. Soc., Chem. Commun. 1970, 935.
504. Brady, W. T. J. Org. Chem. 1966, **31**, 2676.
505. Stevens, H. C.; Rinehart, J. K.; Lavanish, J. M.; Trenta, G. M. J. Org. Chem. 1971, **36**, 2780.
506. Rey, M.; Huber, U. A.; Dreiding, A. S. Tetrahedron Lett. 1968, 3583.
507. Rehn, K.; Dehmer, K.; Roechling, H. Ger. Offen. DE 2,428,410, 1976 [C. A. 1975, **85**, 46093r].
508. Deprés, J. P.; Greene, A. E.; Crabbé, P. Tetrahedron, 1981, **37**, 621.
509. Brady, W. T.; Hoff, E. F., Jr. J. Org. Chem. 1970, **35**, 3733.

510. Brook, P. R.; Harrison, J. M.; Duke, A. J. J. Chem. Soc., Chem. Commun. 1970, 589.
511. Brook, P. R.; Duke, A. J.; Harrison, J. M.; Hunt, K. J. Chem. Soc., Perkin Trans. 1 1974, 927.
512. Brook, P. R.; Duke, A. J.; Duke, J. R. C. J. Chem. Soc., Chem. Commun. 1970, 574.
513. Berson, J. A.; Patton, J. W. J. Am. Chem. Soc. 1962, **84**, 3406.
514. Blomquist, A. T.; Kwiatek, J. J. Am. Chem. Soc. 1951, **73**, 2098.
515. Brooks, B. T.; Wilbert, G. J. Am. Chem. Soc. 1941, **63**, 870.
516. Brady, W. T.; Roe, R. J. Am. Chem. Soc. 1970, **92**, 4618.
517. Brady, W. T.; Roe, R.; Hoff, E. F.; Parry, F. H. J. Am. Chem. Soc. 1970, **92**, 146.
518. Brady, W. T.; Holifield, B. M. Tetrahedron 1967, **23**, 4251.
519. Fitjer, L.; Kanschik, A.; Majewski, M. Tetrahedron Lett. 1985, **26**, 5277.
520. Russell, G. A.; Schmitt, K. D.; Mattox, J. J. Am. Chem. Soc. 1975, **97**, 1882.
521. Michel, P.; O'Donnell, M.; Binamé R.; Hesbain-Frisque, A. M.; Ghosez, L.; Declercq, J. P.; Germain, G.; Arte, E.; Van Meerssche, M. Tetrahedron Lett. 1980, **21**, 2577.
522. Owen, M. D. J. Indian Chem. Soc. 1943, **20**, 343 [C. A. 1944, **38**, 3634^7].
523. Staudinger, H.; Meyer, P. J. Helv. Chim. Acta 1924, **7**, 19.
524. Dawson, T. L.; Ramage, G. R. J. Chem. Soc. 1950, 3523.
525. Cossement, E.; Binamé, R.; Ghosez, L. Tetrahedron Lett. 1974, 997.
526. Rellensmann, W.; Hafner, K. Chem. Ber. 1962, **95**, 2579.
527. Brady, W. T.; Ting, P. L. J. Org. Chem. 1974, **39**, 763.
528. Brady, W. T.; Hieble, J. P. J. Am. Chem. Soc. 1972, **94**, 4278.
529. Brady, W. T.; Parry, F. H.; Roe, R.; Hoff, E. F. Tetrahedron Lett. 1970, 819.
530. Ohshiro, Y.; Ishida, M.; Shibata, J.; Minami, T.; Agawa, T. Chem. Lett. 1982, 587.
531. Staudinger, H. Ber. 1907, **40**, 1145.
532. Lewis, J. R.; Ramage, G. R.; Wainwright, J. L.; Simonsen W. G. J. Chem. Soc. 1937, 1837.
533. Dao, L. H.; Hopkinson, A. C.; Lee-Ruff, E. Tetrahedron Lett. 1978, 1413.
534. Brady, W. T.; Giang, Y. F. J. Org. Chem. 1986, **51**, 2145.
535. Carpino, L. A.; Gund, P.; Springer, J. P.; Gund, T. Tetrahedron Lett. 1981, **22**, 371.
536. Brady, W. T.; Ting, P. L. J. Chem. Soc., Perkin Trans. 1 1975, 456.
537. Lee-Ruff, E.; Ablenas, F. J. Can. J. Chem. 1987, **65**, 1663.

538. Chung, Y. S.; Kruk, H.; Barizo, O. M.; Katz, M.; Lee-Ruff, E. J. Org. Chem. 1987, **52**, 1284.
539. Jutz, C.; Rommel, I.; Lengyel, I.; Feeney, J. Tetrahedron 1966, **22**, 1809.
540. Asao, T.; Machiguchi, T.; Kitamura, T.; Kitahara, Y. J. Chem. Soc., Chem. Commun. 1970, 89.
541. Paquette, L. A.; Andrews, D. R.; Springer, J. P. J. Org. Chem. 1983, **48**, 1147.
542. Gordon, E. M.; Plu ··/ ec, J.; Ondetti, M. A. Tetrahedron Lett. 1981, **22**, 1871.
543. Tanaka, K.; Yoshikoshi, A. Tetrahedron 1971, **27**, 4889.
544. Au-Yeung, B.; Fleming, I. J. Chem. Soc., Chem. Commun. 1977, 79.
545. Fleming, I.; Au-Yeung, B. Tetrahedron 1981, **37**, Supplement No. 1, 13.
546. Goldschmidt, Z.; Antebi, S. Tetrahedron Lett. 1978, 271.
547. Kuroda, S.; Asao, T. Tetrahedron Lett. 1977, 285.
548. Grieco, P. A.; Hiroi, K. Tetrahedron Lett. 1974, 3467.
549. Fleming, I.; Williams, R. V. J. Chem. Soc., Perkin Trans. 1 1981, 684.
550. Greenlee, M. L. J. Am. Chem. Soc. 1981, **103**, 2425.
551. Friedrichsen, W.; Debaerdemaeker, T.; Böttcher, A.; Hahnemann, S.; Schmidt, R. Z. Naturforsch., Teil B 1983, **38**, 504.
552. Harding, K. E.; Strickland, J. B.; Pommerville, J. J. Org. Chem. 1988, **53**, 4877.
553. Kato, M.; Kido, F.; Wu, M. D.; Yoshikoshi, A. Bull. Chem. Soc. Jpn. 1974, **47**, 1516.
554. Grieco, P. A.; Oguri, T.; Gilman, S.; DeTitta, G. T. J. Am. Chem. Soc. 1978, **100**, 1616.
555. Grieco, P. A.; Oguri, T.; Wang, C. L. J.; Williams, E. J. Org. Chem. 1977, **42**, 4113.
556. Baldwin, J. E.; Kapecki, J. A. J. Am. Chem. Soc. 1970, **92**, 4868.
557. Isaacs, N. S.; Hatcher, B. G. J. Chem. Soc., Chem. Commun. 1974, 593.
558. Gheorghiu, M. D.; Pârvulescu, L.; Drâghici, C.; Elian, M. Tetrahedron, 1981, **37**, Supplement No. 1, 143.
559. Farooq, M. O.; Abraham, N. A. Bull. Soc. Chim. Fr. 1958, 832.
560. Greene, A. E.; Lansard, J. P.; Luche, J. L.; Petrier, C. J. Org. Chem. 1983, **48**, 4763.
561. Leriverend, M. L.; Vazeux, M. J. Chem. Soc., Chem. Commun. 1982, 866.
562. Baldwin, J. E.; Breckinridge, M. F.; Johnson, D. S. Tetrahedron Lett. 1972, 1635.

563. Gott, P. G.; French Patent 1,414,456, 1965 [C. A. 1966, **64**, 6523f].

564. Brook, P. R.; Harrison, J. M.; Hunt, K. J. Chem. Soc., Chem. Commun. 1973, 733.

565. Bertrand, M.; Gras, J. L.; Goré, J. Tetrahedron Lett. 1972, 2499.

566. Bertrand, M.; Gras, J. L.; Goré, J. Tetrahedron 1975, **31**, 857.

567. Bertrand, M.; Gras, J. L.; Gil, G. Tetrahedron Lett. 1974, 37.

568. Bampfield, H. A.; Brook, P. R. J. Chem. Soc., Chem. Commun. 1974, 171.

569. Bertrand, M.; Maurin R.; Gras, J. L C. R. Acad. Sci. Paris, Série C 1968, **267**, 417.

570. Brady, W. T.; Stockton, J. D.; Patel, A. D. J. Org. Chem. 1974, **39**, 236.

571. Bampfield, H. A.; Brook, P. R. J. Chem. Soc., Chem. Commun. 1974, 172.

572. Gras, J. L.; Maurin, R.; Bertrand, M. Tetrahedron Lett. 1969, 3533.

573. Weyler, W.; Byrd, L. R.; Caserio, M. C.; Moore, H. W. J. Am. Chem. Soc. 1972, **94**, 1027.

574. Boan, C.; Skattebøl, L. J. Chem. Soc., Perkin Trans. 1 1978, 1568.

575. Bertrand, M; Gras, J. L. Tetrahedron 1974, **30**, 793.

576. Opitz, G.; Zimmermann, F. Justus Liebigs Ann. Chem. 1963, **662**, 178.

577. Hasek, R. H.; Martin, J. C. J. Org. Chem. 1961, **26**, 4775.

578. Hasek, R. H.; Martin, J. C. J. Org. Chem. 1963, **28**, 1468.

579. Martin, J. C. U.S. Patent 3,297,705, 1967 [C. A. 1967, **67**, 99998z].

580. Otto, P.; Feiler, L. A.; Huisgen, R. Angew. Chem., Int. Ed. Engl. 1968, **7**, 737.

581. Huisgen, R.; Otto, P. J. Am. Chem. Soc. 1969, **91**, 5922.

582. Opitz, G.; Kleemann, M.; Zimmermann, F. Angew. Chem. 1962, **74**, 32.

583. Martin, J. C.; Gott, P. G.; Hostettler, H. U. J. Org. Chem. 1967, **32**, 1654.

584. Martin, J. C. J. Org. Chem. 1965, **30**, 4311.

585. Opitz, G.; Adolph, H.; Kleemann, M.; Zimmermann, F. Angew. Chem. 1961, **73**, 654.

586. Hünig, S.; Hoch, H. Chem. Ber. 1972, **105**, 2216.

587. Buysch, H. J.; Hünig, S. Angew. Chem., Int. Ed. Engl. 1966, **5**, 128.

588. Hünig, S.; Hoch, H. Tetrahedron Lett. 1966, 5215.

589. Hassner, A.; Haddadin, M. J.; Levy, A. B. Tetrahedron Lett. 1973, 1015.

590. Sieja, J. B. J. Am. Chem. Soc. 1971, **93**, 130.

591. Hurd, C. D.; Kimbrough, R. D. J. Am. Chem. Soc. 1960, **82**, 1373.

592. Lee-Ruff, E.; Chung, Y. S. J. Heterocycl. Chem. 1986, **23**, 1551.

593. Effenberger, F.; Fischer, P.; Prossel, G.; Kiefer, G. Chem. Ber. 1971,

104, 1987.

594. Bisceglia, R. H.; Cheer, C. J. J. Chem. Soc., Chem. Commun. 1973, 165.
595. Potman, R. P.; Janssen, N. J. M. L.; Scheeren, J. W.; Nivard, R. J. F. J. Org. Chem. 1984, **49**, 3628.
596. Huisgen, R.; Feiler, L.; Binsch, G. Angew. Chem., Int. Ed. Engl. 1964, **3**, 753.
597. Huisgen, R.; Feiler, L.; Binsch, G. Angew. Chem. 1964, **76**, 892.
598. Martin, J. C.; Goodlett, V. W.; Burpitt, R. L. J. Org. Chem. 1965, **30**, 4309.
599. Fráter, G.; Müller, U.; Günther, W. Helv. Chim. Acta 1986, **69**, 1858.
600. Krepski, L. R.; Hassner, A. J. Org. Chem. 1978, **43**, 3173.
601. Vedejs, E.; Larsen, S. D. J. Am. Chem. Soc. 1984, **106**, 3030.
602. Pirrung, M. C.; DeAmicis, C. V. Tetrahedron Lett. 1988, **29**, 159.
603. Shipov, A. G.; Savost'yanova, I. A.; Zaitseva, G. S.; Baukova, Y. I.; Lutsenko, I. F. Zh. Obshch. Khim. 1977, **47**, 1198 [C. A. 1977, **87**, 85078a].
604. Cocuzza, A. J.; Boswell, G. A. Tetrahedron Lett. 1985, **26**, 5363.
605. Annis, G. D.; Paquette, L. A. J. Am. Chem. Soc. 1982, **104**, 4504.
606. Marino, J. P.; Neisser, M. J. Am. Chem. Soc. 1981, **103**, 7687.
607. Greene, A. E.; Charbonnier, F. Tetrahedron Lett. 1985, **26**, 5525.
608. Martin, J. C. U.S. Patent 3,410,892, 1968 [C. A. 1969, **70**, 28475c].
609. Gompper, R.; Studeneer, A.; Elser, W. Tetrahedron Lett. 1968, 1019.
610. Scarpati, R.; Sica, D.; Santacroce, C. Tetrahedron 1964, **20**, 2735.
611. Brady, W. T.; Watts, R. D. J. Org. Chem. 1981, **46**, 4047.
612. Zaitseva, G. S.; Bsukov, Y. I.; Mal'tsev, V. V.; Lutsenko, I. P. Zh. Obshch. Khim. 1974, **44**, 1415 [C. A. 1974, **81**, 105619j].
613. Bell š, D.; Fischer, H.; Greuter, H; Martin, P. Helv. Chim. Acta 1978, **61**, 1784.
614. Bell š, D. J. Am. Chem. Soc. 1978, **100**, 8026.
615. Brady, W. T.; Saidi, K. J. Org. Chem. 1980, **45**, 727.
616. Scarpati, R.; Sica, D. Rend. Acad. Sci. Fis. Mat., Naples 1961, **28**, 70 [C. A. 1965, **62**, 6425a].
617. Habibi, M. H.; Saidi, K.; Sams, L. C. J. Fluorine Chem. 1987, **37**, 177.
618. Brady, W. T.; Giang, Y. F. J. Org. Chem. 1985, **50**, 5177.
619. Snider, B. B.; Hui, R. A. H. F.; Kulkarni, Y. S. J. Am. Chem. Soc. 1985, **107**, 2194.
620. Snider, B. B.; Hui, R. A. H. F. J. Org. Chem. 1985, **50**, 5167.
621. Maujean, A.; Marcy, G.; Chuche, J. J. Chem. Soc., Chem. Commun.

1980, 92.

622. Leyendecker, F.; Bloch, R.; Conia, J. M. Tetrahedron Lett. 1972, 3703.
623. Leyendecker, F. Tetrahedron 1976, **32**, 349.
624. Aryal-Kaloustian, S.; Wolff, S.; Agosta, W. C. J. Org. Chem. 1978, **43**, 3314.
625. Kulkarni, Y. S.; Burbaum, B. W.; Snider, B. B. Tetrahedron Lett. 1985, **26**, 5619.
626. Markó, I.; Ronsmans, B.; Hesbain-Frisque, A. M.; Dumas, S.; Ghosez, L.; Ernst, B.; Greuter, H. J. Am. Chem. Soc. 1985, **107**, 2192.
627. Snider, B. B.; Kulkarni, Y. S. J. Org. Chem. 1987, **52**, 307.
628. Baldwin, S. W.; Page, E. H. J. Chem. Soc., Chem. Commun. 1972, 1337.
629. Veenstra, S. J.; De Mesmaeker, A.; Ernst, B. Tetrahedron Lett. 1988, **29**, 2303.
630. Yadav, J. S.; Joshi, B. V.; Gadgil, V. R. Indian J. Chem., Sect. A 1987, **26B**, 399 [C. A. 1988, **108**, 131097h].
631. Snider, B. B.; Niwa, M. Tetrahedron Lett. 1988, **29**, 3175.
632. Goldschmidt, Z.; Gutman, U.; Bakal, Y.; Worchel, A. Tetrahedron Lett. 1973, 3759.
633. Mori, K.; Miyake, M. Tetrahedron 1987, **43**, 2229.
634. Kulkarni, Y. S.; Snider, B. B. J. Org. Chem. 1985, **50**, 2809.
635. Beereboom, J. J. J. Org. Chem. 1965, **30**, 4230.
636. Beereboom, J. J. J. Am. Chem. Soc. 1963, **85**, 3525.
637. Lee, S. Y.; Niwa, M.; Snider, B. B. J. Org. Chem. 1988, **53**, 2356.
638. Corey, E. J.; Desai, M. C. Tetrahedron Lett. 1985, **26**, 3535.
639. Sauers, R. R.; Kelly, K. W. J. Org. Chem. 1970, **35**, 3286.
640. De Mesmaeker, A.; Veenstra, S. J.; Ernst, B. Tetrahedron Lett. 1988, **29**, 459.
641. Becker, D.; Nagler, M.; Birnbaum, D. J. Am. Chem. Soc. 1972, **94**, 4771.
642. Murray, R. K.; Goff, D. L.; Ford, T. M. J. Org. Chem. 1977, **42**, 3870.
643. Moon, S.; Kolesar, T. F. J. Org. Chem. 1974, **39**, 995.
644. Quinkert, G.; Kleiner, E.; Freitag, B. J.; Glenneberg, J; Billhardt, U. M.; Cech, F.; Schmieder, K. R.; Schudok, C.; Steinmetzer, H. C.; Bats, J. W.; Zimmerman, G.; Dürner, G.; Rehm, D.; Paulus, E. F. Helv. Chim. Acta 1986, **69**, 469.
645. Gleiter, R.; Kissler, B.; Ganter, C. Angew. Chem., Int. Ed. Engl. 1987, **26**, 1252.
646. Sasaki, T.; Eguchi, S.; Hirako, Y. J. Org. Chem. 1977, **42**, 2981.
647. Snider, B. B.; Beal, R. B. J. Org. Chem. 1988, **53**, 4508.

648. Yates, P.; Fallis, A. G. Tetrahedron Lett. 1968, 2493.
649. Becker, D.; Harel, Z.; Birnbaum, D. J. Chem. Soc., Chem. Commun. 1975, 377.
650. Funk, R. L.; Novak, P. M.; Abelman, M. M. Tetrahedron Lett. 1988, **29**, 1493.
651. Kuwajima, I.; Higuchi, Y.; Iwasawa, H.; Sato, T. Chem. Lett. 1976, 1271.
652. Ireland, R. E.; Dow, W. C.; Godfrey, J. D.; Thaisrivongs, S. J. Org. Chem. 1984, **49**, 1001.
653. Smit, A.; Kok, J. G. J.; Geluk, H. W. J. Chem. Soc., Chem. Commun. 1975, 513.
654. Oppolzer, W.; Nakao, A. Tetrahedron Lett. 1986, **27**, 5471.
655. Hart, H.; Love, G. M. J. Am. Chem. Soc. 1971, **93**, 6266.
656. Masamune, S.; Fukumoto, K. Tetrahedron Lett. 1965, 4647.
657. Corey, E. J.; Desai, M. C.; Engler, T. A. J. Am. Chem. Soc. 1985, **107**, 4339.
658. Ireland, R. E.; Godfrey, J. D.; Thaisrivongs, S. J. Am. Chem. Soc. 1981, **103**, 2446.
659. Ireland, R. E.; Aristoff, P. A. J. Org. Chem. 1979, **44**, 4323.
660. Knoche, H. Justus Liebigs Ann. Chem. 1969, **722**, 232.
661. England, D. C.; Krespan, C. J. Org. Chem. 1970, **35**, 3308.
662. Martin, J. C. U.S. Patent 3,408,398, 1968 [C. A. 1969, **70**, 19658n].
663. Gheorghiu, M. D.; Drăghici, C.; Stanescu, L.; Avram, M. Tetrahedron Lett. 1973, 9.
664. Smith, L. I.; Hoehn, H. H. J. Am. Chem. Soc. 1941, **63**, 1175.
665. Kinugasa, K.; Agawa, T. Organomet. Chem. Synth. 1972, **1**, 427.
666. Wong, H. N.; Sondheimer, F.; Goodin, R.; Breslow, R. Tetrahedron Lett. 1976, 2715.
667. Springer, J. P.; Clardy, J.; Cole, R. I.; Kirkney, J. W.; Hill, R. K.; Carlson, R. M.; Isidor, J. L. J. Am. Chem. Soc. 1974, **96**, 2268.
668. Ried, W.; Kraemer, R. Justus Liebigs Ann. Chem. 1965, **681**, 52.
669. Johns, R. B.; Kreigler, A. B. Aust. J. Chem. 1964, **17**, 765.
670. Canonica, L.; Corbella, A.; Jommi, G.; Pelizzoni, F.; Scholastico, C. Tetrahedron Lett. 1966, 3031.
671. Dorsey, D. A.; King, S. M.; Moore, H. W. J. Org. Chem. 1986, **51**, 2814.
672. Rosebeek, B.; Arens, J. F. Recl. Trav. Chim. Pays-Bas 1962, **81**, 549.
673. Pericas, M.; Serratosa, F.; Valenti, E. Synthesis 1985, 1118.
674. Daalen, J. J.; Kraak, A.; Arens, J. F. Recl. Trav. Chim. Pays-Bas 1961, **80**, 810.
675. Danheiser, R. L.; Gee, S. K. J. Org. Chem. 1984, **49**, 1672.

676. Danheiser, R. L.; Gee, S. K.; Perez, J. J. J. Am. Chem. Soc. 1986, **108**, 806.

677. Truce, W. E.; Bavry, R. H.; Bailey, P. S. Tetrahedron Lett. 1968, 5651.

678. Kuehne, M. E.; Sheehan, P. J. J. Org. Chem. 1968, **33**, 4406.

679. Henn, L.; Himbert, G.; Diehl, K.; Kaftory, M. Chem. Ber. 1986, **119**, 1953.

680. Himbert, G. J. Chem. Res. (S) 1978, 104.

681. Himbert, G.; Schwickerath, W. Justus Liebigs Ann. Chem. 1984, 85.

682. Himbert, G. J. Chem. Res. (S) 1978, 442.

683. Henn, L.; Himbert, G. Chem. Ber. 1981, **114**, 1015.

684. Wheeler, E. N.; Fisher, G. J. U.S. Patent 3,029,253, 1962 [C. A. 1962, **57**, 7970c].

685. Nagato, S.; Kato, R. Yuki Gosei Kagaku Kyokai Shi 1970, **28**, 326 [C. A. 1970, **73**, 44855u].

686. Nagato, S.; Omori, Y.; Kato, R. Yuki Gosei Kagaku Kyokai Shi 1970, **28**, 243 [C. A. 1970, **72**, 110735n].

687. Schilling, B.; Eberle, H. Ger. Offen. DE 3227108 A1, 1984 [C. A. 1984, **100**, 156482c].

688. Newman, M. S.; Leegwater, A. J. Org. Chem. 1968, **33**, 2144.

689. Oshe, H.; Palm, R.; Cherdron, H. Monatsh. Chem. 1967, **98**, 2138.

690. Schimmelschmidt, Mundlos, E. Ger. DE 1,136,323, 1960 [C. A. 1963, **58**, 3321d].

691. Del'tsova, D. P.; Koshtoyan, S. O.; Zeifman, Y. V. Izv. Akad. Nauk SSSR, Ser. Khim. 1970, 2140 [C. A. 1971, 76378c].

692. Bormann, D.; Wegler, R. Chem. Ber. 1969, **102**, 64.

693. Reich, D. A.; Stevens, H. C. U.S. Patent 3,719,689, 1973 [C. A. 1973, **78**, 136991s].

694. Nakajima, K.; Yamashita, A. Jpn. Kokai JP 76 56445, 1976 [C. A. 1976, **85**, 176859f].

695. Nakajima, K.; Yamashita, A.; Okamoto, S. Jpn. Kokai JP 76 59850, 1976 [C. A. 1976, **85**, 93868g].

696. White, E. in Smith, C. W. *Acrolein*, Wiley, New York, 1962.

697. McCain, J. H.; Marcus, E. J. Org. Chem. 1970, **35**, 2414.

698. Brady, W. T.; Saidi, K. J. Org. Chem. 1979, **44**, 733.

699. Fomina, T. B.; Artem'eva, V. N.; Sazanov, Y. N. Zh. Org. Khim. 1971, **7**, 2295 [C. A. 1972, **76**, 59154a].

700. Fomina, T. B.; Artem'eva, V. N.; Sozanov, Y. N.; Koton, M. M. Dokl. Akad. Nauk SSSR 1970, **193**, 838 [C. A. 1975, **73**, 99247c].

701. Higuchi, H.; Arimoto, K. Jpn. Kokai Tokkyo Koho, 73 00462, 1973.

702. Ishida, M.; Minami, T.; Agawa, T. J. Org. Chem. 1979, **14**, 2067.
703. Takasu, I.; Higuchi, M.; Suzuki, R. Jpn. Kokai JP 75 05191, (1975) [C. A. 1975, **83**, 131238v].
704. Kondo, K.; Ryu, Y. Jpn. Kokai JP 77 06977, 1977 [C. A. 1973, **78**, 29239f].
705. Kondo, K.; Ryu, Y.; Dobashi, S. Jpn. Kokai JP Tokkyo Koho 74 61153, 1974.
706. Kondo, K.; Ryu, Y. Jpn. Kokai Tokkyo Koho JP 73 61420, 1973.
707. Kondo, K.; Ryu, Y. Jpn. Kokai Tokkyo Koho JP 77 020969, 1977 [C. A. 1974, **80**, 59469q].
708. Achmatowicz, O.; Leplawy, M. Bull. Akad. Polon. Sci., Ser. Sci., Chem. Geol. Geograph. 1958, **6**, 417 [C. A. 1959, **53**, 3183g].
709. Zubovics, Z.; Ishikawa, N. J. Fluorine Chem. 1976, **8**, 43.
710. Chse, H.; Pilgrim, K. Tetrahedron Lett. 1968, 1949.
711. Pilgrim, K.; Ohse, H. J. Org. Chem. 1969, **34**, 1586.
712. Knunyants, I. L.; Cheburkov, Y. A. Bull. Acad. Sci. USSR. Div. Chem. Sci. 1961, 747 [C. A. 1960, **54**, 22349c].
713. Bergman, E.; Cohen, S.; Hoffman, E.; Rand-Meir, Z. J. Chem. Soc. 1961, 3452.
714. Cornforth, R. H. J. Chem. Soc. 1959, 4052.
715. England, D. C.; Krespan, C. G. J. Org. Chem. 1968, **33**, 816.
716. Wiley, R. H. U.S. Patent 3,356,721, 1967 [C. A. 1968, **68**, 49085z].
717. Knunyants, I. L.; Gambaryan, N.; Tyuleneva, V. Izv. Akad. Nauk SSSR, Ser. Khim. 1967, 2662 [C. A. 1968, **69**, 67299x].
718. Staudinger, H. Ber. 1908, **41**, 1355.
719. Sazonov, Y. N.; Glukhov, N. A.; Koton, M. M. Dokl. Akad. Nauk SSSR 1967, **177**, 363 [C. A. 1968, **69**, 2559n].
720. Rosowski, A.; Tarbell, D. S. J. Org. Chem. 1961, **26**, 2255.
721. Cornforth, J. W.; Cornforth, R. H.; Pelter, A.; Horning, M. G.; Popjak, G. Tetrahedron 1959, **5**, 311.
722. Reid, W.; Bellinger, O. Justus Liebigs Ann. Chem. 1984, 1778.
723. Agranat, I.; Cohen, S.; Aharon-Shalom, E.; Bergmann, E. Tetrahedron 1975, **31**, 1163.
724. Brady, W. T.; Gu, Y. J. Org. Chem. 1988, **53**, 1353.
725. Staudinger, H. Helv. Chim. Acta 1918, **3**, 862.
726. Brady, W. T.; Patel, A. D. J. Chem. Soc., Chem. Commun. 1971, 1642.
727. Van Der Puy, M.; Anello, L. C.; Sukornick, B.; Sweeney, R.; Wiles, R. A. U.S. Patent 4,244,891, 1981 [C. A. 1981, **94**, 208337p].
728. Eiden, F.; Peglow, M. Arch. Pharm. (Weinheim, Ger.) 1970, **303**, 61 [C.

A. 1970, **72**, 78797w].

729. Gompper, R.; Studeneer, A.; Elser, W. Tetrahedron Lett. 1968, 1019.
730. Nazarov, I. N.; Kuznetsov, N. V. J. Gen. Chem. USSR (Eng. Transl.) 1959, **29**, 754.
731. Kitahara, Y.; Oda, M.; Kayama, Y. Angew. Chem. 1976, **88**, 536.
732. Morita, N.; Asao, T. Chem. Lett. 1973, 67.
733. Asao, T.; Morita, N.; Iwagame, N. Bull. Chem. Soc. Jpn. 1974, **47**, 773.
734. Wittig, G.; Hesse, A. Justus Liebigs Ann. Chem. 1976, 500.
735. Morita, N.; Asao, T.; Kitahara, Y. Tetrahedron Lett. 1974, 2083.
736. Higuchi, M.; Suzuki, A. Jpn. Kokai, 74 25,942.
737. Goldschmidt, Z.; Antebi, S. Tetrahedron Lett. 1978, 1225.
738. Staudinger, H.; Kon, N. Justus Liebigs Ann. Chem. 1912, **384**, 38.
739. Morita, N.; Asao, T. Chem. Lett. 1975, 71.
740. Neidlein, R.; Salzl, M. Arch. Pharm. (Weinheim, Ger.) 1977, **310** 685 [C. A. 1978, **88**, 6637b].
741. Markl, G.; Hauptmann, H. Tetrahedron 1978, **32**, 2131.
742. Hastings, J. S.; Heller, H. G.; Salisbury, K. J. Chem. Soc., Perkin Trans. 1 1975, 1995.
743. Kuroda, S.; Ojima, J.; Kitatani, K.; Kirita, M.; Nakada, T. Chem. Soc., Perkin Trans. 1 1983, 2987.
744. Kuroda, S.; Kitatani, K.; Ojima, J. Tetrahedron Lett. 1982, **23**, 2657.
745. Asao, T.; Morita, N.; Ojima, J.; Fujiyoshi, M. Tetrahedron Lett. 1978, 2795.
746. Ojima, J.; Itagawa, K.; Hamai, S.; Nakada, T.; Kuroda, S. J. Chem. Soc., Perkin Trans. 1 1983, 2997.
747. Gilman, H.; Adams, C. E. Recl. Trav. Chim. Pays-Bas 1929, **48**, 464.
748. Heller, H. G.; Auld, D.; Salisbury, K. J. Chem. Soc. (C) 1967, 1552.
749. Eiden, F.; Peglow, M. Arch. Pharm. (Weinheim, Ger.) 1970, **303**, 825 [C. A. 1971, **74**, 3460p].
750. Hastings, J. S.; Heller, H. G. J. Chem. Soc., Perkin Trans. 2 1972, 1839.
751. Hastings, J. S.; Heller, H. G.; Tucker, H.; Smith, K. J. Chem. Soc., Perkin Trans. 1 1975, 1545.
752. Staudinger, H. Ber. 1908, **41**, 1493.
753. Augustin, M.; Kohler, M. Z. Chem. 1983, **23**, 402.
754. Neidlein, R.; Bernhard, E. Justus Liebigs Ann. Chem. 1979, 959.
755. Neidlein, R.; Kraemer, A. D. Angew. Chem. 1977, **89**, 48.
756. Neidlein, R.; Kraemer, A. D. J. Heterocycl. Chem. 1977, **14**, 1369.
757. Agranat, I.; Pick, M. Tetrahedron Lett. 1973, 4079.

758. Ojima, J.; Kuroda, S.; Kirita, M. Chem. Lett. 1982, 1371.
759. Heller, H. G.; Auld, D.; Salisbury, K. J. Chem. Soc. (C) 1967, 682.
760. Markl, G.; Olbrich, H. Angew. Chem. 1966, **78**, 598.
761. Tanaka, K.; Toda, F. Tetrahedron Lett. 1980, **21**, 2713.
762. Fuchs, R. Ger. Offen. DE 2,634,540, 1977 [C. A. 1978, **88**, 89136m].
763. Ebnöther, A.; Jucker, E.; Rissi, E.; Rutschmann, J.; Schreier, E.; Steiner, R.; Süess, R.; Vogel, A. Helv. Chim. Acta 1959, **42**, 918.
764. Poshkus, A. C.; Herweh, J. E. J. Org. Chem. 1965, **30**, 2466.
765. Staudinger, H.; Göhring, O.; Scholler, M. Chem. Ber. 1914, **47**, 40.
766. Saito, T.; Oikawa, I.; Motoki, S. Bull. Chem. Soc. Jpn. 1980, **53**, 2582.
767. Boosen, K. J.; Azer, N. Swiss Patent CH 602,554, 1978 [C. A. 1978, **89**, 214910h].
768. Birkofer, L.; Lukenhaus, W. Justus Liebigs Ann. Chem. 1984, 1193.
769. Metzger, C.; Kurz, J. Chem. Ber. 1971, **104**, 50.
770. Brady, W. T.; Dorsey, E. D.; Parry, F. H. J. Org. Chem. 1969, **34**, 2846.
771. Hull, R. J. Chem. Soc. (C) 1967, 1154.
772. Brady, W. T.; Owens, R. A. Tetrahedron Lett. 1976, 1553.
773. Brady, W. T.; Dorsey, E. D. J. Chem. Soc., Chem. Commun. 1968, 1638.
774. Brady, W. T.; Dorsey, E. D. J. Org. Chem. 1970, **35**, 2732.
775. Huisgen, R.; Funke, E.; Schaefer, F.; Knorr, R. Angew. Chem. 1967, **79**, 321.
776. Funke, E.; Huisgen, R. Chem. Ber. 1971, **104**, 3222.
777. Weyler, W.; Duncan, W. G.; Moore, H. W. J. Am. Chem. Soc. 1975, **97**, 6187.
778. Moore, H. W.; Chow., K.; Nguyen, N. J. Org. Chem. 1987, **52**, 2530.
779. Talaty, E. R.; Dupuy, A. E.; Untermoehlen, C. M.; Sterkoll, L. H. J. Chem. Soc., Chem. Commun. 1973, 48.
780. Minami, T.; Yamakata, K.; Ohshiro, Y.; Agawa, T.; Yasuoka, N.; Kasai, N. J. Org. Chem. 1972, **37**, 3810.
781. Grill, H.; Kresze, G. Tetrahedron Lett. 1970, 1427.
782. Makarov, S. P.; Shpanskii, V. A.; Ginsberg, V. A.; Shchekotikhin, A. I.; Filatov, A. S.; Martynova, L. L.; Pavlovskaya, I. V.; Golovaneva A. F.; Yakubovich, A. Y. Dokl. Akad. Nauk SSSR 1961, **142**, 596 [C. A. 1962, **57**, 4228a].
783. Staudinger, H.; Jelagin, S. Ber. 1911, **44**, 365.

783a. Hall, J.; Krishnan, G. J. Org. Chem. 1984, **49**, 2498.
784. Bird, C. W. Chem. Ind. (London) 1963, 1556.

785. Kerber, R. C.; Ryan, T. J. Tetrahedron Lett. 1970, 703.

786. Kerber, R. C.; Ryan, T. J.; Hsu, S. D. J. Org. Chem. 1974, **39**, 1215.

787. Colonna, M.; Risalti, A. Gazz. Chim. Ital. 1960, **90**, 1165 [C. A. 1958, **52**, 377c].

788. Cook, A. H.; Jones, D. G. J. Chem. Soc. 1941, 184.

789. Fischer, W.; Fahr, E. Tetrahedron Lett. 1966, 5245.

790. Brooks, G.; Shaw, M. A.; Taylor, G. A. J. Chem. Soc., Perkin Trans. 1 1973, 1297.

791. Yamamoto, A.; Abe, I.; Nozawa, M.; Kotani, M.; Motoyoshiya, J.; Gotoh, H.; Matsuzaki, K. J. Chem. Soc., Perkin Trans. 1 1983, 2297.

792. Horner, L.; Spietschka, E. Chem. Ber. 1956, **89**, 2765.

793. Fahr, E.; Büttner, E.; Keil, K. H.; Markert, J.; Schenkenbach, F.; Thiedemann, R.; Fontaine, J. Justus Liebigs Ann. Chem. 1981, 1433.

794. Oshiro, Y.; Komatsu, M.; Yamamoto, Y.; Takari, K.; Agawa, T. Chem. Lett. 1974, 383.

795. Kirmse, W. Chem. Ber. 1960, **93**, 2357.

796. Staudinger, H.; Anthes, E.; Pfenninger, F. Ber. 1916, **49**, 1928.

797. L'abbé, G.; Verhelst, G.; Yu, C.; Toppet, S. J. Org. Chem. 1975, **40**, 1728.

798. Mohan, S.; Kumar, B.; Sandhu, J. Chem. Ind. (London) 1971, 671.

799. Del'tsova, D. P.; Gambaryan, N. P. Izv. Akad. Nauk SSSR, Ser. Khim. 1976, 858 [C. A. 1976, **85**, 123732c].

800. Katagiri, N.; Niwa, R.; Kato, T. Heterocycles 1983, **20**, 597.

801. Sakamoto, M.; Miyazawa, K.; Yamamoto, K.; Tomimatsu, Y. Chem. Pharm. Bull. 1974, **22**, 2201.

802. Bödeker, J.; Courault, K. Tetrahedron 1978, **34**, 101.

803. Mazumdar, S. N.; Ibnusaud, I.; Mahajan, M. P. Tetrahedron Lett. 1986, **27**, 5875.

804. Ried, W.; Radt, W. Justus Liebigs Ann. Chem. 1964, **676**, 110.

805. Ried, W.; Radt, W. Angew. Chem., Int. Ed. Engl. 1963, **2**, 397.

806. Erickson, J. L. E.; Dechary, J. M. J. Am. Chem. Soc. 1952, **74**, 2644.

807. Schönberg, A.; Mustafa, A. J. Chem. Soc. 1947, 997.

808. Bignardi, G.; Evangelisti, F.; Schenone, P.; Bargagna, A. J. Heterocycl. Chem. 1972, **9**, 1071.

809. Bargagna, A.; Cafaggi, S.; Schenone, P. J. Heterocycl. Chem. 1977, **14**, 249.

810. Schenone, P.; Bargagna, A.; Bignardi, G.; Evangelisti, F. J. Heterocycl. Chem. 1976, **13**, 1105.

811. Bignardi, G.; Schenone, P.; Evangelisti, F. Ann. Chim. (Rome) 1971, **61**,

326 [C. A. 1971, **75**, 129608g].

812. Mosti, L.; Menozzi, G.; Schenone, P. J. Heterocycl. Chem. 1984, **21**, 361.
813. Mosti, L.; Schenone, P.; Menozzi, G.; Romussi, G.; Baccichetti, F.; Carlassare F.; Bordin, F. Il Farmaco (Ed. Sci.) 1984, **39**, 81 [C. A. 1983, **99**, 88080d].
814. Mosti, L.; Schenone, P.; Menozzi, G. J. Heterocycl. Chem. 1980, **17**, 61.
815. Schenone, P.; Evangilisti, F.; Bignardi, G.; Bargagna, A. Ann. Chim. (Rome) 1974, **64**, 613 [C. A. 1976, **84**, 121596s].
816. Bargagna, A.; Schenone, P.; Bondavalli, F.; Longobardi, M. J. Heterocycl. Chem. 1980, **17**, 33.
817. Menozzi, G.; Mosti, L.; Schenone, P. J. Heterocycl. Chem. 1983, **20**, 539.
818. Bignardi, G.; Mosti, L.; Schenone, P.; Menozzi, G. J. Heterocycl. Chem. 1977, **14**, 1023.
819. Bargagna, A.; Cafaggi, S.; Schenone, P. J. Heterocycl. Chem. 1980, **17**, 507.
820. Bargagna, A.; Schenone, P.; Bondavalli, F.; Longobardi, M. J. Heterocycl. Chem. 1982, **19**, 257.
821. Bargagna, A.; Evangilisti, F.; Schenone, P. J. Heterocycl. Chem. 1981, **18**, 111.
822. Mosti, L.; Menozzi, G.; Schenone, P. J. Heterocycl. Chem. 1981, **18**, 1263.
823. Bargagna, A.; Evangilisti, F.; Schenone, P. J. Heterocycl. Chem. 1979, **16**, 93.
824. Mosti, L.; Bignardi, G.; Evangelisti, F.; Schenone, P. J. Heterocycl. Chem. 1976, **13**, 1201.
825. Cafaggi, S.; Romussi, G.; Ciarallo, C.; Bignardi, G. Il Farmaco (Ed. Sci.) 1983, **38**, 775 [C. A. 1984, **100**, 68199k].
826. Bargagna, A.; Schenone, P.; Bondavalli, F.; Longobardi, M. J. Heterocycl. Chem. 1980, **17**, 1201.
827. Mosti, L.; Schenone, P.; Menozzi, G. J. Heterocycl. Chem. 1979, **16**, 913.
828. Meslin, J. C.; Quiniou, H. C. R. Acad. Sci. Paris, Série C 1971, **273**, 148.
829. Okazaki, R.; Sunagawa, K.; Kang, K.; Inamoto, N. Bull. Chem. Soc. Jpn. 1979, **52**, 496.
830. Meslin, J. C. C. R. Acad. Sci. Paris, Série C 1973, **277**, 1391.
831. Meslin, J. C.; Pradere, J. P.; Quiniou, H. Bull. Soc. Chim. Fr. 1976, 1195.
832. Karakasa, T.; Yamaguchi, H.; Motoki, S. J. Org. Chem. 1980, **45**, 927.
833. Kollenz, G.; Ziegler, E.; Ott, W.; Kriwetz, G. Z. Naturforsch., Teil B 1977,

32, 701.

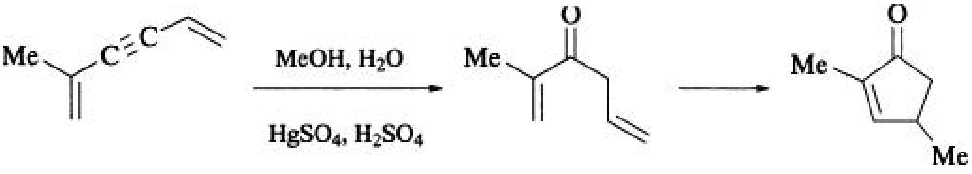
834. Kollenz, G.; Ziegler, E.; Ott, W. Org. Prep. Proc. Int. 1973, **5**, 261.
835. Kollenz, G.; Igel, H.; Ziegler, E. Monatsh. Chem. 1972, **103**, 450.
836. Ziegler, E.; Ott, W. Synthesis 1973, 679.

The Nazarov Cyclization

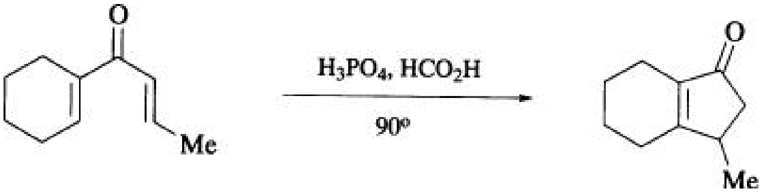
Karl L. Habermas, University of Illinois, Urbana, Illinois
Scott E. Denmark, University of Illinois, Urbana, Illinois
Todd K. Jones, Ligand Pharmaceuticals Inc., San Diego, California

1. Introduction

The Nazarov cyclization is named after the eminent Russian chemist I. N. Nazarov (1900–1957). In the course of an extensive study on the formation of allyl vinyl ketones by the mercuric ion and acid-catalyzed hydration of dienynes, Nazarov and his co-workers discovered a secondary reaction to form 2-cyclopentenones (Eq. 1). (1-38) Nazarov initially formulated a direct acid-catalyzed closure of the allyl vinyl ketones and demonstrated the preparation of 2-cyclopentenones from these precursors in dozens of cases. However in 1952, Braude and Coles (39) suggested the intermediacy of carbocations and demonstrated that the formation of 2-cyclopentenones actually proceeds via the α , α ′-divinyl ketones. This fact, together with further mechanistic clarification, has led to the current formulation of the Nazarov cyclization as the acid-catalyzed closure of divinyl ketones to 2-cyclopentenones.

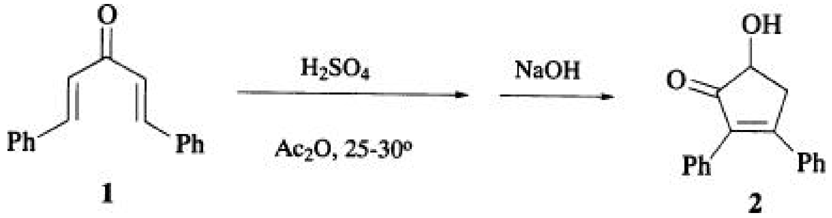


(1)



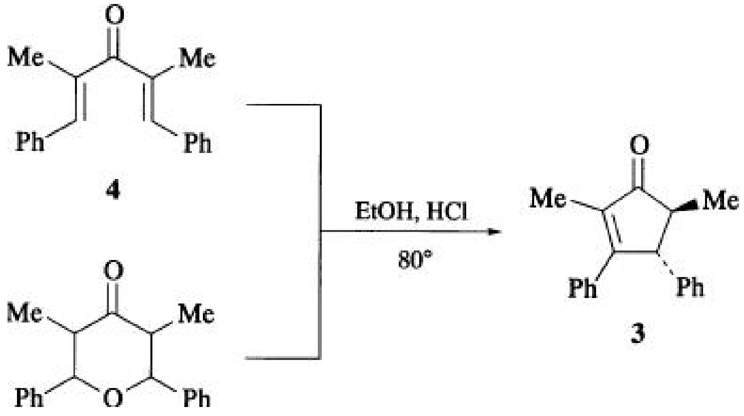
(2)

This process was already documented in 1903. (40) Treatment of dibenzylideneacetone (**1**) with concentrated sulfuric acid and acetic anhydride followed by mild alkaline hydrolysis afforded a ketol **2**, the correct structure of which was finally proposed in 1955 (Eq. 3). (41) Other examples of acid-catalyzed cyclizations of divinyl ketones exist in the early literature, as do reactions which must have proceeded via divinyl ketones. (42, 43)



(3)

A broader definition of the Nazarov cyclization includes a wide variety of precursors that under specific reaction conditions also produce 2-cyclopentenones via divinyl ketones or their functional equivalents. A case in point is the formation of cyclopentenone **3** by treatment of either divinyl ketone **4** or tetrahydropyrone **5** with ethanolic hydrochloric acid (Eq. 4). (44) It is the structural variety of precursors that lends versatility to the Nazarov cyclization and which also serves as the organizational framework for this chapter.



(4)

To facilitate presentation, the reaction is divided into six categories defined by the structure of the precursor: (1) cyclization of divinyl and allyl vinyl ketones, (2) cyclization of silylated (stannylated) divinyl ketones, (3) in situ generation/cyclization of divinyl ketones or equivalents, (4) generation/cyclization of divinyl ketone equivalents by solvolysis, (5) alkyne-based precursors of divinyl ketones, and (6) coupling reactions to form and cyclize divinyl ketones. The logic of this sequence follows from the order of decreasing structural similarity of the precursors to divinyl ketones. This review is intended to be comprehensive in the coverage of cyclizations which produce 2-cyclopentenones. The related electrocyclic closure of less oxidized pentadienylic cations (45) is not covered. The reaction was most recently reviewed in 1991. (46) Prior to that, the Nazarov cyclization had been reviewed in 1983 (47) and also in the context of pentannulation. (48, 49)

2. Mechanism and Stereochemistry

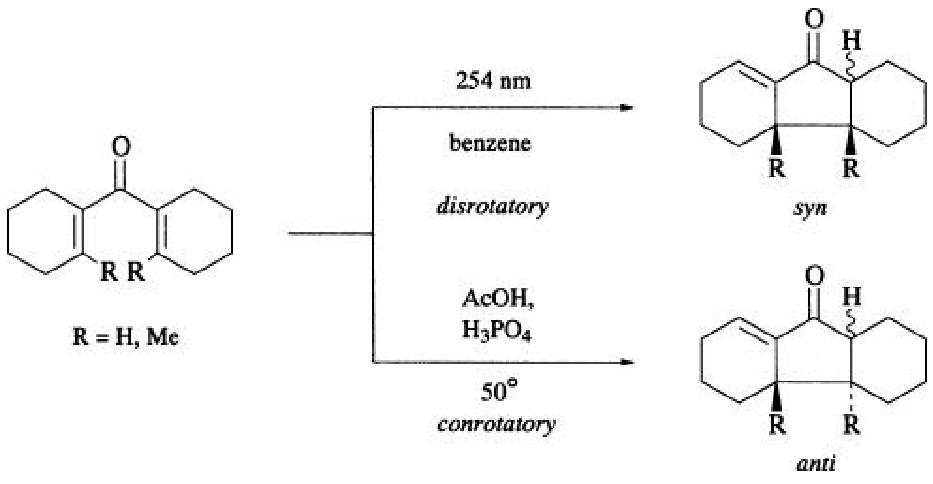
The first reasonable proposals for the mechanism of the Nazarov cyclization suggested the intermediacy of a β ketocarbocation from *C*-protonation of either divinyl or allyl vinyl ketones. (39) The ring is formed by intramolecular attack on the enone with concomitant generation of an α -ketocarbocation. Loss of a β proton from this intermediate affords the product. Nazarov provided support for this proposal by demonstrating the incorporation of deuterium from D_3PO_4 in different positions from divinyl or allyl vinyl ketones. (32, 35, 36)

From both stereochemical and spectroscopic studies it is now well established that the Nazarov cyclization is a pericyclic reaction belonging to the class of electrocyclizations, specifically a 4 π electrocyclic closure of a 3-hydroxypentadienylic cation. (50) Simple pentadienylic cations had been observed early on to undergo facile cyclization to cyclopentenylic cations. (51, 52) More recently, the *O*-protonated divinyl ketones and the cyclopentenone rearrangement products have been spectroscopically observed. (53) Moreover, the intermediacy of carbocations is consistent with the observation of Wagner–Meerwein rearrangement products and anomalous cyclization pathways.

As with all pericyclic reactions, mechanism and stereochemistry are intimately coupled. Thus discussion of one feature must invoke the other. Therefore, for a clear description of the mechanism, the stereospecific (54) aspects of the Nazarov cyclization are discussed below.

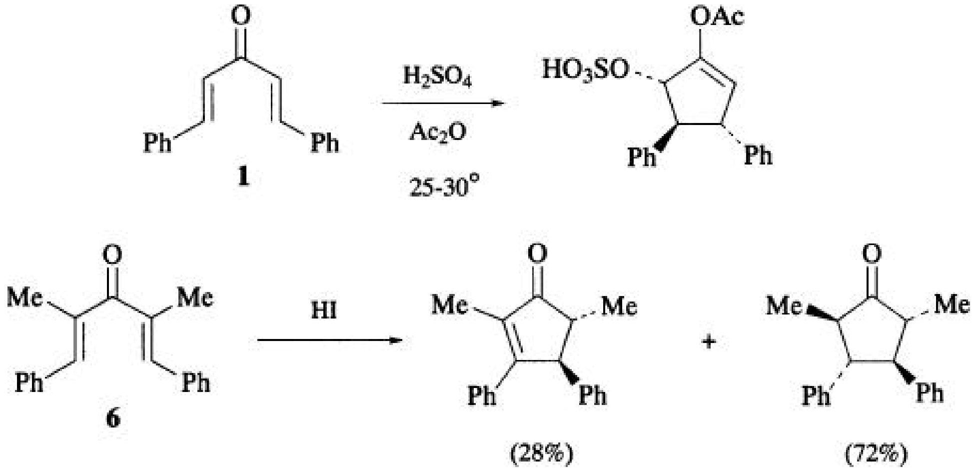
The basic tenets of the theory of electrocyclic reactions (50) makes very clear predictions about the relative configuration of the substituents on the newly formed bond of the five-membered ring. Unfortunately, secondary rearrangements thwarted early attempts to verify the stereochemical predictions of orbital symmetry control in the parent system. (52) Subsequent studies with the pentamethyl derivatives were successful. (55, 56)

The most convincing evidence for a pericyclic mechanism was the demonstration of complementary rotatory pathways for the thermal (conrotatory) and photochemical (disrotatory) cyclizations of bis(1-cyclohexenyl)ketones (Eq. 5) precisely as predicted by the conservation of orbital symmetry. (57)



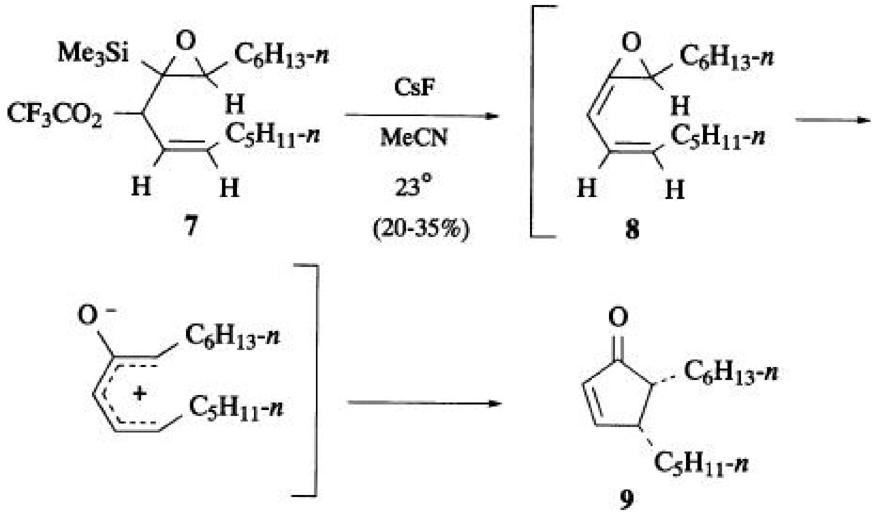
(5)

Additional confirmation came from reinvestigation of the early work on the thermal cyclization of dibenzylideneacetone (**1**) (58) and dibenzylidene-3-pentanone (**6**) (44) in the presence of acid. Careful examination revealed the conrotatory electrocyclic pathway for both of these substrates.



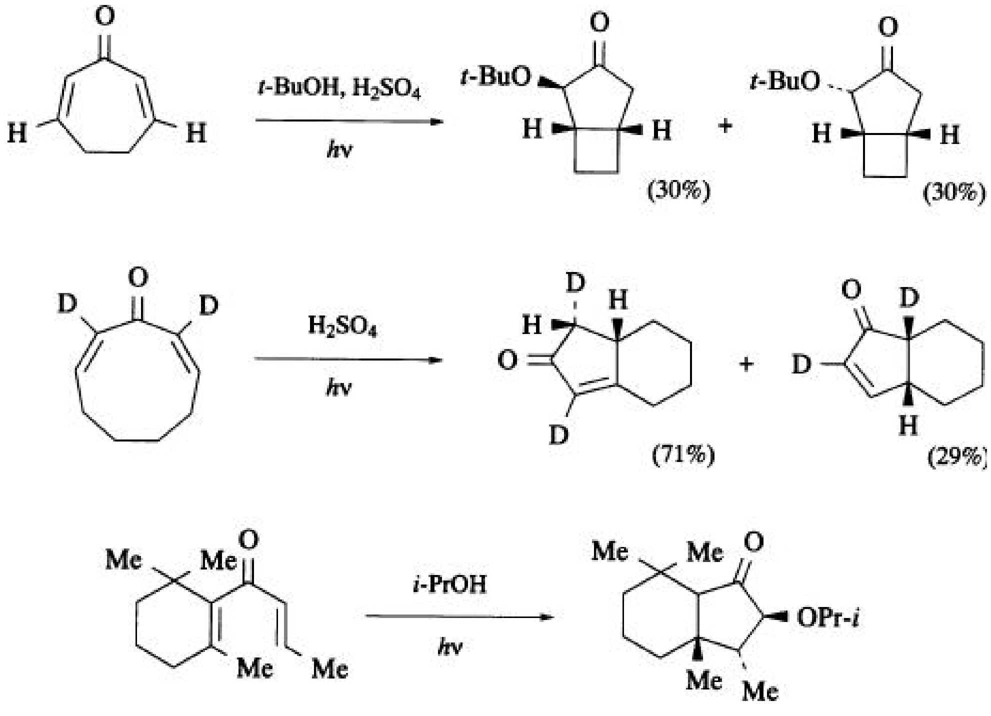
(6)

The rules for conservation of orbital symmetry also predict a change in the configuration of the products from either a given cyclization mode or a permutation of starting olefin geometry. This prediction is difficult to test under the normal reaction conditions (acid, light) that would isomerize dienone double bonds. However, fluoride treatment of the silyl epoxide **7** leads to the formation of the *cis*-disubstituted cyclopentenone **9** from a *Z,E* precursor, the putative allene oxide **8**, which cyclizes via the 2-oxido pentadienylic cation. (59)



(7)

The predicted photochemical disrotatory closure of protonated divinyl ketones has been documented in several laboratories. (60-62) The examples in Eq. 8 show

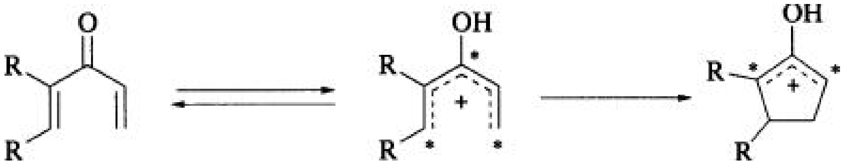


(8)

how secondary processes allowed for determination of the sense of electrocyclization, for example, cation quenching and hydride or alkyl migration.

A theoretical study of the Nazarov cyclization has evaluated the relative stability of the 3-oxopentadienylic cation and the product cyclopentenylic cations. The lowest energy conformation was the *syn–anti* isomer and the overall reaction was found to be exothermic by 2.3 kcal/mol. A transition state was also located corresponding to an activation enthalpy of 20.6 kcal/mol. The C(1)–C(5) distance is 2.09 Å in the transition structure. (63, 64)

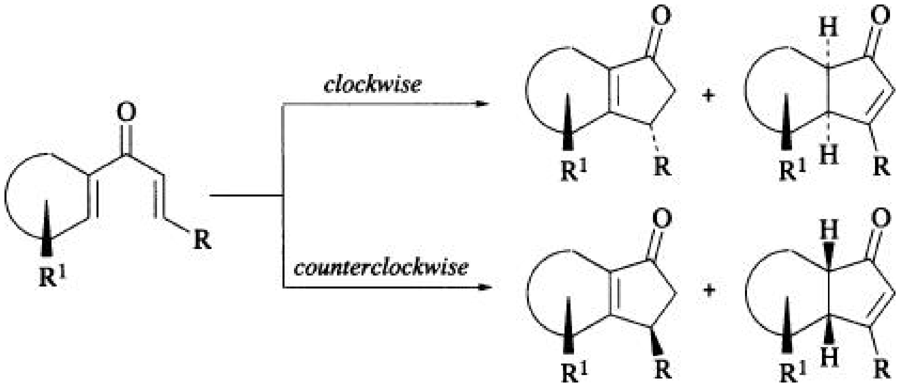
The cationic electrocyclization mechanism allows prediction of substituent effects. In the rate-limiting step, the distribution of positive charge changes from C(1), C(3), and C(5) in the pentadienylic cation to C(2) and C(4) in the cyclopentenylic cation (Eq. 9). Thus substituents that stabilize positive charge should accelerate



(9)

(αposition) or decelerate (β position) the electrocyclization depending upon location. Moreover, the effects for α substitution should be greater in magnitude for groups of similar stabilizing capacity since the charge is less delocalized. This empirical analysis has been verified experimentally as well as theoretically by Mulliken population analysis. (64)

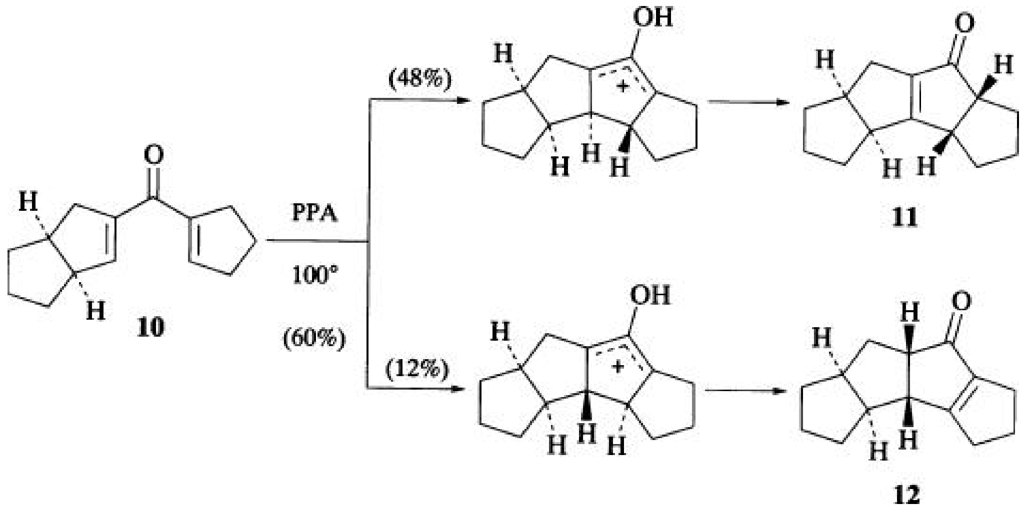
Beyond the mechanistically mandated stereochemical imperative of conrotatory or disrotatory closure, there exists a secondary stereochemical feature that arises because of the duality of allowed electrocyclization pathways. This feature, called torquoselectivity, (65) is manifest when the divinyl ketone is chiral by virtue of a remote substituent, and the two pathways lead to diastereomers (Eq. 10). The



(10)

nature of the relationship between the newly created centers and preexisting centers depends upon the location of the cyclopentenone double bond. In the classical cyclization, the double bond normally occupies the most substituted position, corresponding to a Saytzeff elimination process. The sense of rotation is defined by clockwise (*R*) rotation or counterclockwise (*S*) rotation viewing down the C -O bond. Thus, depending on the final placement of the double bond, the newly created center may be proximal or distal to the preexisting center.

The factors that control the sense of torquoselection in the Nazarov cyclization are primarily steric in origin. Most significant are the torsional and nonbonded interactions between the substituents in the vicinity of the newly forming bond during the electrocyclization event. The phosphoric acid induced closure of triquinane **10** in Eq. 11 illustrates the stereochemical consequences of opposite conrotatory closures. (66) Interestingly the major product **11** arises from bond formation on the concave face of the diquinane unit.



(11)

3. Scope and Limitations

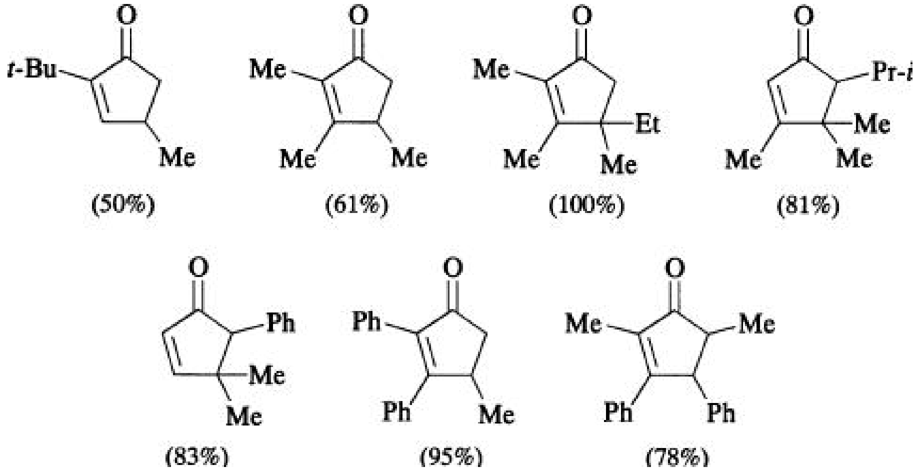
3.1. Divinyl and Allyl Vinyl Ketones

The tautomeric divinyl and allyl vinyl ketones are équivalent precursors for acid-promoted cyclization. Deuterium-labeling studies established the isomerization of the allyl to a vinyl group prior to cyclization. (32, 35, 36) The preparation of these substrates differs, however, since most allyl vinyl ketones are produced by the mercuric ion catalyzed hydration of dienynes, which in turn are prepared by dehydration of vinylacetylide adducts of ketones. This approach allows for the incorporation of many substituents. Since divinyl ketones are implied as intermediates in other variants of the Nazarov cyclization, only those reactions where a divinyl ketone is used directly are discussed below.

3.1.1.1. Acyclic Precursors

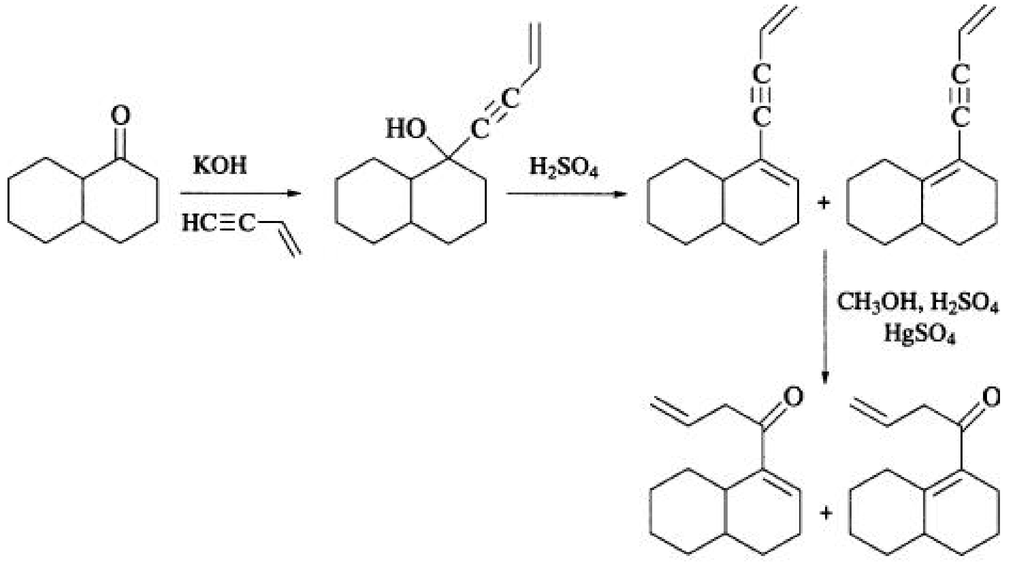
Simple cyclopentenones have been prepared in modest to good yield using the Nazarov cyclization. Many substitution patterns are available by this protocol, most commonly 2,3,4-trisubstituted and 2,3,4,4-tetrasubstituted 2-cyclopentenones. The usually vigorous reaction conditions (phosphoric acid, heat) lead to the thermodynamically most stable cyclopentenone double bond isomer. Aromatic substituents are compatible with the reaction conditions and have a beneficial effect on the yield and, in the α position, on the rate as well.

Figure 1.

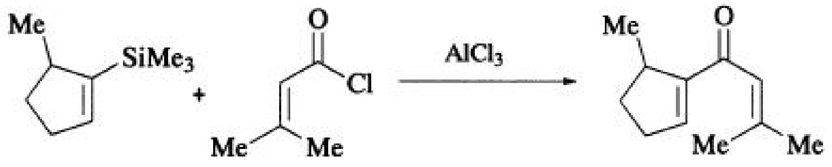


3.1.1.2. Monocyclic Precursors

The Nazarov cyclization has been extensively used as a cyclopentenone annulation method. For the construction of fused cyclic systems, one of the groups attached to the ketone must be cyclic. Classically, this was accomplished by vinylacetylide addition to cycloalkanones followed by dehydration and alkyne hydrolysis (Eq. 12). However, with unsymmetrically



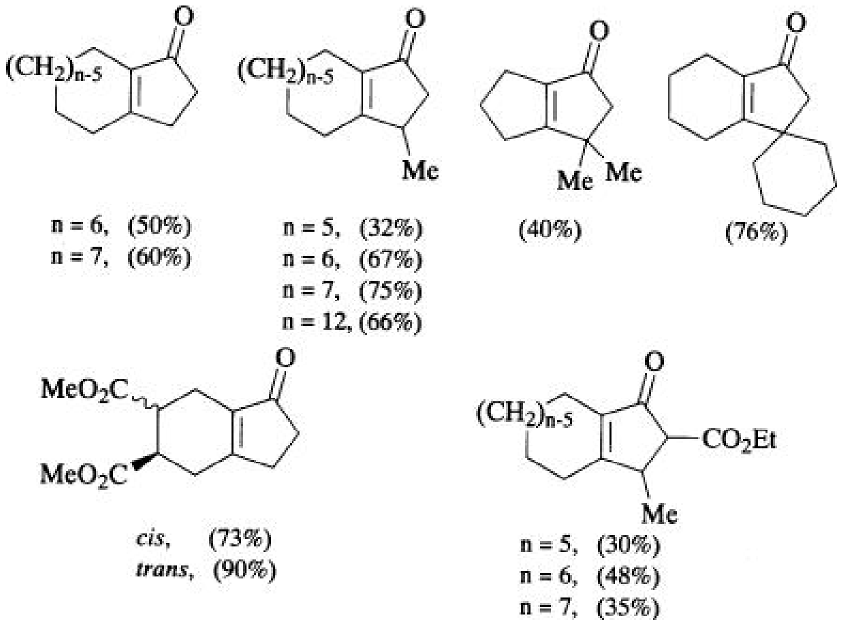
(12)



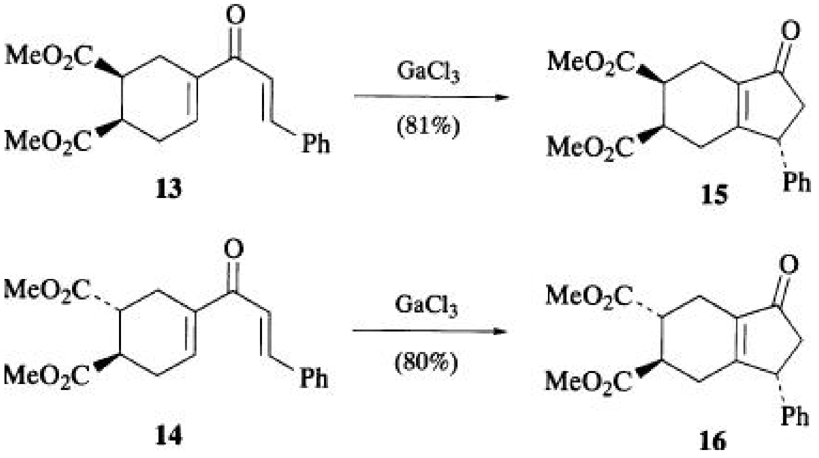
substituted cycloalkanones, regioisomers are formed. (11, 22) An alternative construction, based on the acylation of cycloalkenylsilanes, provides divinyl ketones with predictable structure. (67, 68)

Annulations onto preexisting rings of 5, 6, 7, and 12 members have been reported. The yields are generally lowest for 5-membered rings. The vinyl (allyl) appendage can accommodate substituents on both α and β positions as well as β , β′ disubstitution. The compatibility of ester and imide functional groups is also noteworthy. 69,69a,70

Figure 2.



The issue of torquoselectivity is illustrated, in the cyclization of the *cis* and *trans* diesters **13** and **14**. In each case a single diastereomer of the ring fusion unsaturated isomers **15** and **16** is produced (Eq. 13). (70)

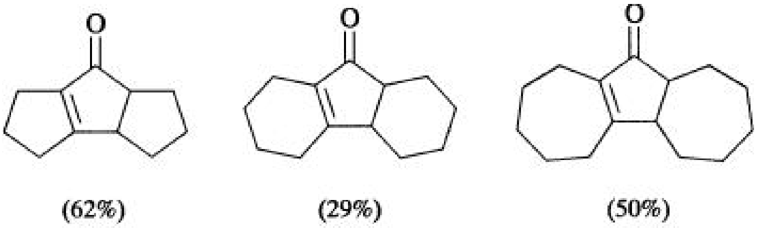


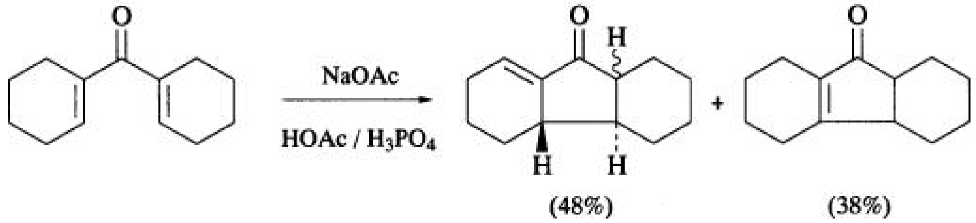
(13)

3.1.1.3. Bis Cyclic Precursors

Formation of a cyclopentenone imbedded in a linear polycyclic array has been accomplished by Nazarov cyclization of bis(cycloalkenyl) ketones. Various combinations of five-, six-, and seven-membered ring systems have been employed. (71, 72) Since the reaction operates under rather harsh conditions, the location of the double bond and the ring fusion stereochemistry are difficult to control.

Figure 3.



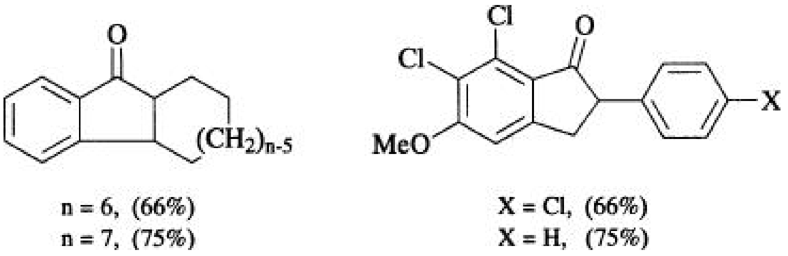


This mode of cyclization has been employed in the establishment of the conrotatory electrocyclization mechanism (57, 73, 74) and in synthetic efforts directed toward trichodiene (75) and ophiobolins. (66)

3.1.1.4. Aromatic Precursors

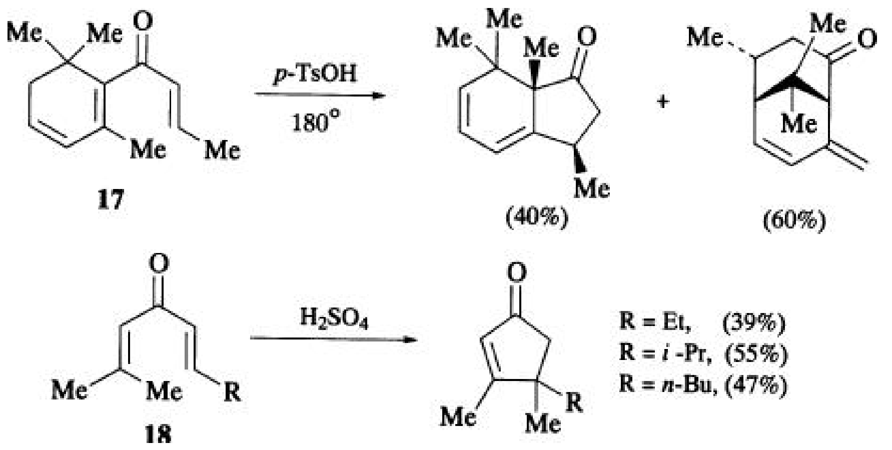
Aryl vinyl ketones can also undergo Nazarov cyclization under sufficiently vigorous conditions. Both monocyclic and bis-cyclic types have been documented. (76, 77) In the monocyclic series, the presence of aromatic substituents at the α position of the vinyl group facilitates cyclization and leads to high yields. (78)

Figure 4.



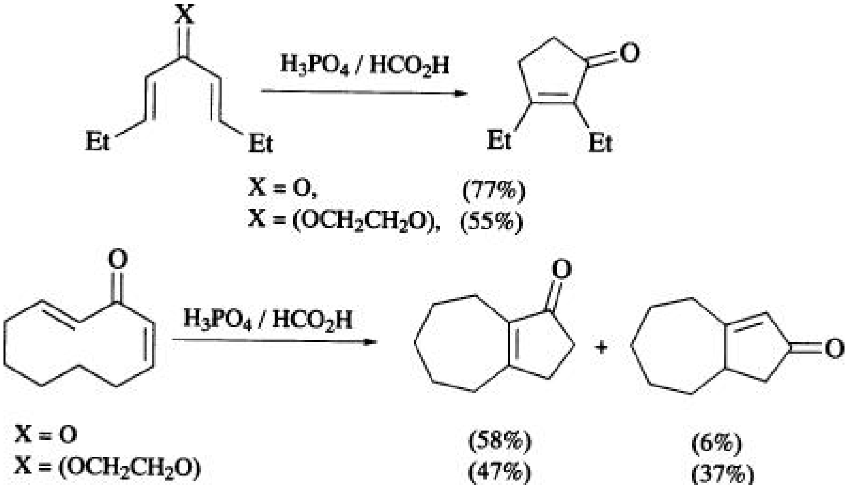
3.1.1.5. Anomalous Cyclizations

The intermediacy of stable carbocations in the Nazarov cyclization has led to the observation of a number of rearrangement products (58) and alternative reaction pathways. Three categories have been identified. The first is simple Wagner–Meerwein rearrangement of the first-formed cyclopentenylic cation. This pathway is characteristic of β , β , β ′-trisubstituted precursors **17** and **18** (Eq. 14). (53, 62)



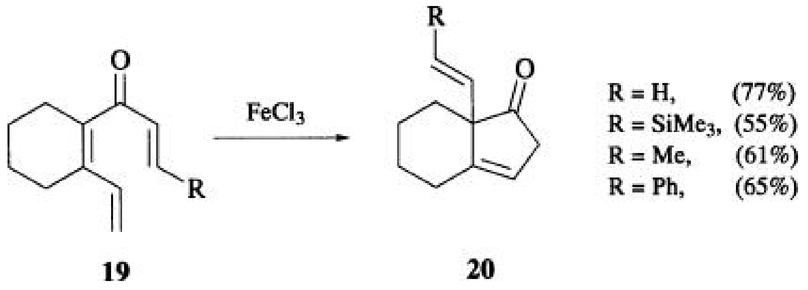
(14)

The second category is the “abnormal” Nazarov cyclization, which affords transposed 2-cyclopentenones arising from nucleophilic capture of the intermediate cyclopentenylic cations with carboxylic acids (Eq. 15). (79, 80) Both ketones and their derived dioxolane acetals have been employed in this transformation. An interesting consequence of this pathway is the production of fused bicyclic ketones from macrocyclic divinyl ketones.



(15)

The third category of anomalous cyclizations involves the intervention of an electrocyclic closure of linearly conjugated dienyl ketones. The monocyclic dienyl vinyl ketones **19** produce exclusively the angularly substituted hydrindenones **20** (Eq. 16). (81) These products must arise from preferential electrocyclic closure of the dienyl ketone followed by rapid Wagner–Meerwein shift of the vinyl group. The substituent effects on rate of rearrangement are consistent with this pathway.



(16)

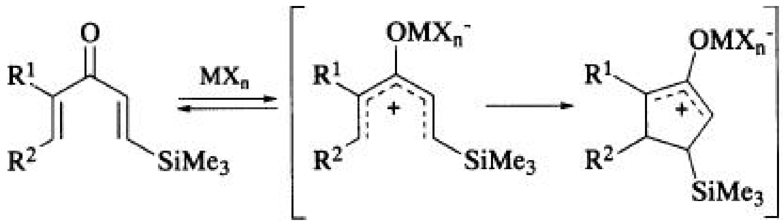
3.1.1.6. Photochemical Cyclizations

Although a number of photo-induced electrocyclic closures of divinyl ketones have been reported, they are of little preparative significance. 60–62,82,82a,82b For the most part these reactions have provided convincing evidence for the electrocyclization mechanism. (73) The products of disrotatory closure are isolated in these cases (see Eqs. 5 and 8). The photoisomerization of 4-pyrones in alcoholic medium affords 5-alkoxy-4-hydroxy-2-cyclopentenones. These products most probably arise from a photo-Nazarov reaction followed by capture of the zwitterionic intermediate (Eq. 17). (83) Intramolecular capture of the zwitterionic intermediate has also been reported. (83a)

(17)

3.2. Silylated (Stannylated) Divinyl Ketones

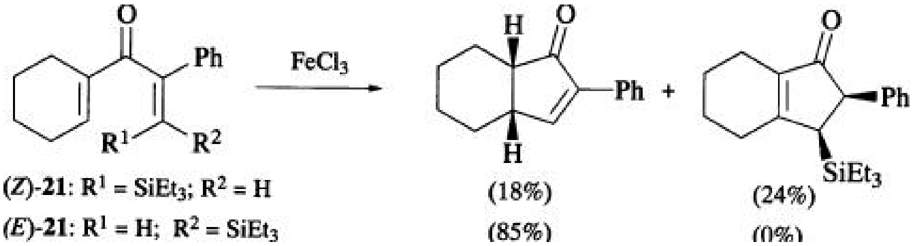
The preparative utility of the Nazarov cyclization is greatly enhanced by employing β -silyl- or α ′-silyldivinyl ketones as precursors. (81, 84-90) The trialkylsilyl groups control the collapse of the intermediate cyclopentenylic cations, (91) thus providing two important benefits: (1) secondary cationic rearrangements are suppressed and (2) the final position of the cyclopentenone double bond is controlled. The latter feature is particularly significant in cyclopentenone annulations with monocyclic precursors because the double bond can be placed in the thermodynamically less stable position, therefore preserving the stereocenters created at the ring fusion.



(18)

3.2.1.1. Vinylsilanes

A number of general methods for the preparation of β -silyldivinyl ketones have been developed. (85, 88, 92-96) Trimethylsilyl groups have been most often employed, though larger alkyl and aryl groups have also been used successfully. (86, 87) The loss of the silicon electrofuge in the cyclization is dependent on the geometry of the β -silylvinyl unit. The triethylsilyl group in *Z*-**21** is partially retained in the product of cyclization, (97) whereas *E*-**21** undergoes highly selective silicon-directed closure (Eq. 19). (98)

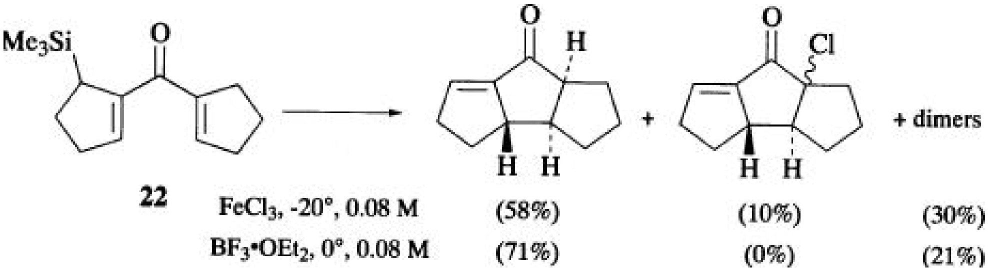


(*Z*)-**21**: R^1 = SiEt$_3$; R^2 = H (18%) (24%)

(*E*)-**21**: R^1 = H; R^2 = SiEt$_3$ (85%) (0%)

(19)

The silicon-directed Nazarov cyclization is effectively promoted by Lewis acids, most commonly anhydrous iron(III) chloride, at temperatures below ambient. (85) For slow reacting substrates, boron trifluoride etherate and zirconium tetrachloride can also be employed where the oxidizing properties of iron(III) chloride are problematic. (88) Even with the extremely reactive α ′-silyl substrates such as **22**, oxidized and chlorinated products can be isolated from reactions with iron(III) chloride at low temperature (Eq. 20). (89)

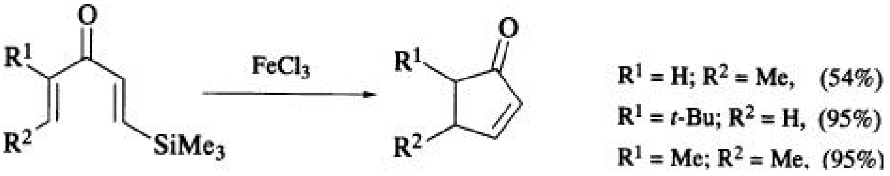


22 FeCl$_3$, -20°, 0.08 M (58%) (10%) (30%)

BF$_3$•OEt$_2$, 0°, 0.08 M (71%) (0%) (21%)

(20)

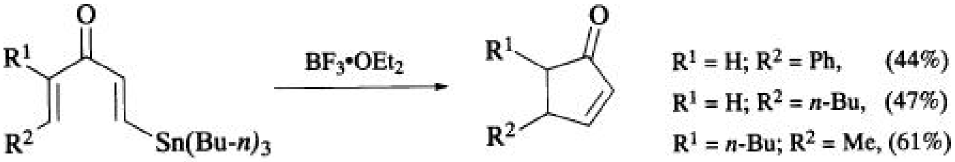
The utility of the silicon-directed Nazarov cyclization is illustrated by the preparation of simple cyclopentenones in which the double bond resides in the least substituted position. Examples of α and β monosubstitution and α , β disubstitution have been described (Eq. 21). (85)



R^1 = H; R^2 = Me, (54%)
R^1 = *t*-Bu; R^2 = H, (95%)
R^1 = Me; R^2 = Me, (95%)

(21)

In an analogous fashion, β -tributylstannyldivinyl ketones **23** are employed for tin-directed Nazarov cyclizations, exclusively in the acyclic mode (Eq. 22). (99)



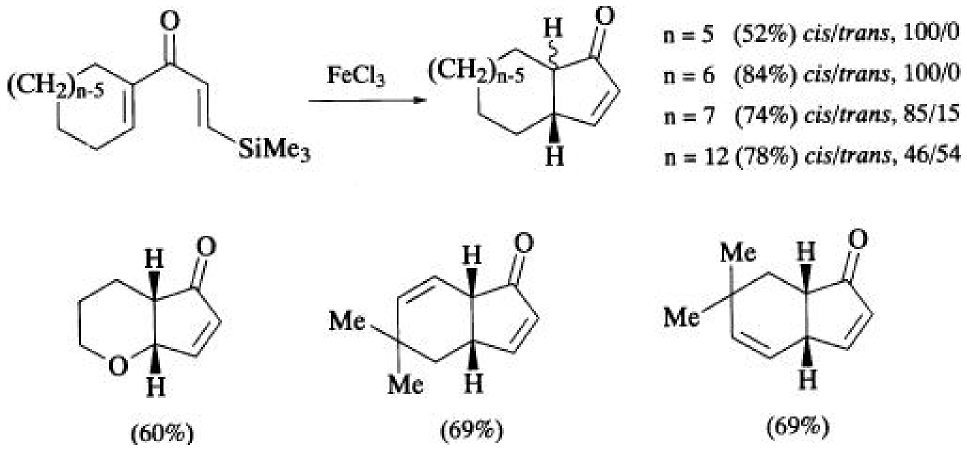
23

R^1 = H; R^2 = Ph, (44%)
R^1 = H; R^2 = *n*-Bu, (47%)
R^1 = *n*-Bu; R^2 = Me, (61%)

(22)

These reactions are best promoted by boron trifluoride etherate. The construction of the substrates by aldol condensation of the β-stannylvinyl ketones is noteworthy.

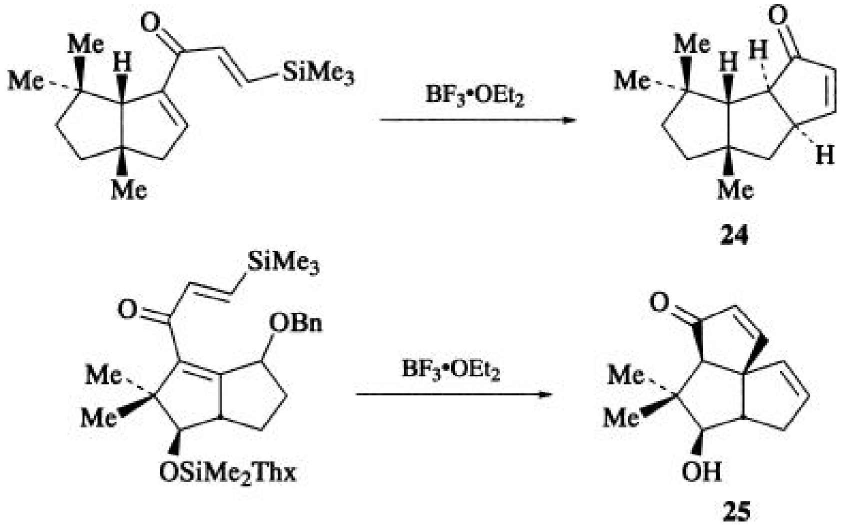
The silicon-directed Nazarov cyclization is ideally suited for cyclopentenone annulation. Precursors containing 5-, 6-, 7-, and 12-membered rings afford bicyclic products in good yields wherein the double bond is exclusively in the less substituted position. (85) The ring fusion is predominantly in the *cis* configuration. Both heterocycles and unsaturated carbocycles can be employed as substrates for the annulation (Eq. 23). (88)



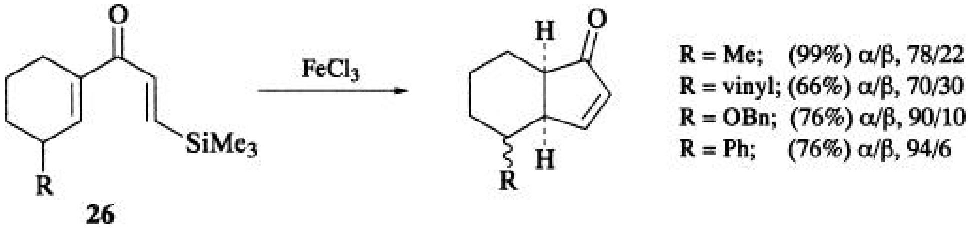
(23)

Cyclopentenone annulation with chiral substrates has been extensively examined. The stereochemical course of conrotatory closure is dependent upon ring size, substituent location, substituent size, and silyl group size. (86-88) In the cyclopentenyl series the selectivity is modest, though construction of linear (**24**) (95) and angular (**25**) 100,100a triquinanes has been reported to proceed with excellent stereoselectivity (Eq. 24).

In the cyclohexenyl series, the directing effect is greatest when substituents are located at the γ position of the endocyclic enone **26** (Eq. 25). (86) The major isomer produced bears a *trans* relationship between the vicinal stereocenters, and the



(24)

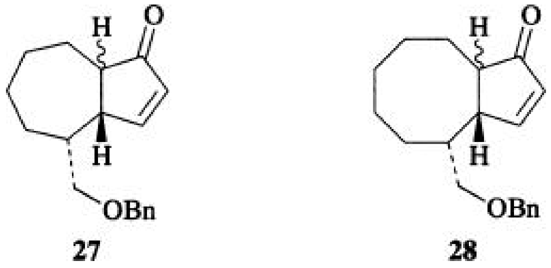


(25)

level of selection is highly dependent upon the substituent size. The bulk of silicon substituents was also shown to have an influence on stereoselectivity. (87)

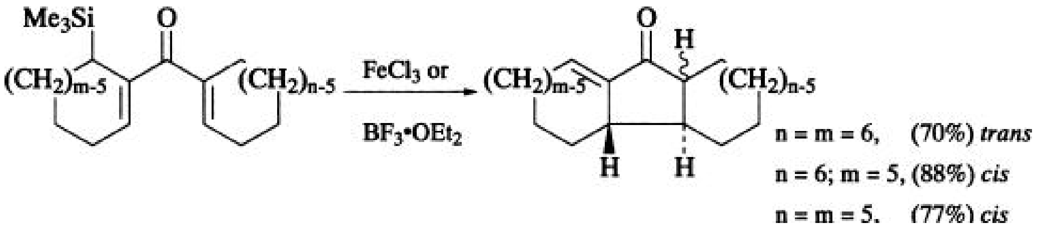
Both cycloheptenyl and cyclooctenyl systems bearing a γ -benzyloxymethyl substituent have been examined and show remarkable levels of stereoselectivity. In these cases, the major product bears a *cis* relationship between the vicinal stereocenters at the ring fusion and the benzyloxymethyl group. The *cis/trans* ratio is 92/8 in **27** and 93/7 in **28**. (98)

Figure 5.



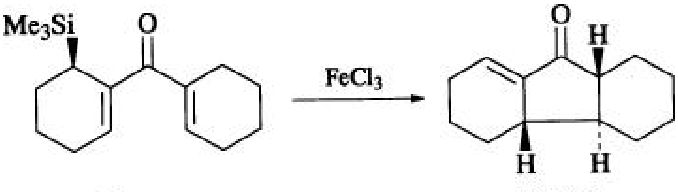
3.2.1.2. Allylsilanes

The use of silicon direction has also been adapted to construction of linearly fused tricyclic systems. (89) In this variant the placement of the double bond is directed away from both ring fusions by placement of the trialkylsilyl group at the α ′ position. These reactions proceed much more rapidly than those of the β -silyldivinyl ketones and are compatible with various combinations of ring sizes (Eq. 26).



(26)

The stereodirecting effect of the remote silicon electrofuge has been demonstrated in the highly stereoselective electrocyclization of an optically active sample of **29** (Eq. 27). (90) The enantiomeric purity and absolute configuration of **30** (as shown) establish the exclusive conrotatory pathway, which corresponds to an *anti* S_E substitution.



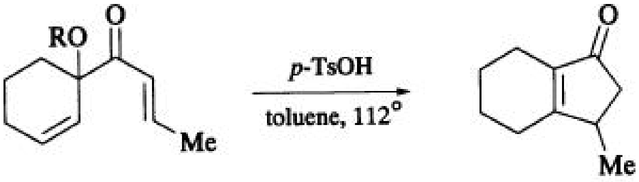
29 88% ee **30** 88% ee

(27)

3.3. In Situ Generation of Divinyl Ketones or Equivalents

3.3.1.1. From α -Alkoxy Enones

Construction of cyclopentenones by the Nazarov cyclization can be effected by generation of divinyl ketones under conditions that effect closure. Of the myriad of precursors of divinyl ketones, the simplest are α ′- and β ′-heterosubstituted, α , β -unsaturated ketones. The α ′-oxygenated enones are readily prepared by the addition of acyl anion equivalents (propenal d^1 reagents) to ketones (Eq. 28). The elimination–cyclization is effected by treatment of the derived tertiary acetates **31** with acid at elevated temperatures. (101) The parent alcohols or silyl ethers are also converted, albeit in lower yield.



31

(28)

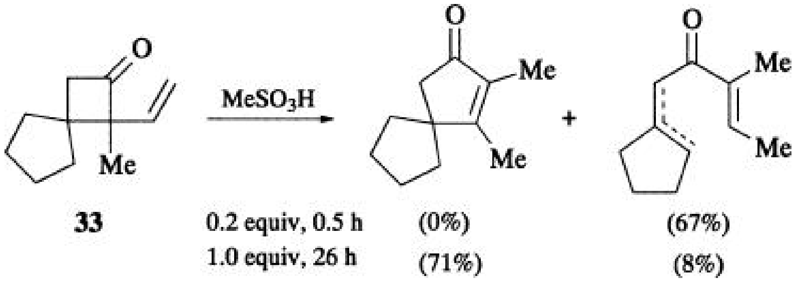
3.3.1.2. From β -Substituted Precursors

β ′-Substituted enones suffer facile βelimination of chlorine, (102, 103) nitrogen, (104) or oxygen groups under acidic conditions required to cyclize the resulting divinyl ketones. The double β elimination of tetrahydro-4-pyranones **32** to form 2-cyclopentenone-4-carboxylates is induced by trimethylsilyl iodide (105) or trimethylsilyl triflate (69a) (Eq. 29). Interestingly, the putative intermediate α -carboalkoxy divinyl ketones have been independently cyclized with trimethylsilyl iodide (69) and triflate. (69a)

(29)

3.3.1.3. *From α -Vinylcyclobutanones*

Divinylketones are also generated by an unusual acid catalyzed rearrangement of α -vinylcyclobutanones. Treatment of β , β -disubstituted α -vinylcyclobutanones **33** with a catalytic amount of boron trifluoride etherate or methanesulfonic acid results in the formation of ring opened divinyl ketones. By the use of a full equivalent of acid, the cyclopentenone is the major product (Eq. 30). The reaction is of limited preparative value as four different classes of products have been identified arising from different substitution patterns. (106-108)

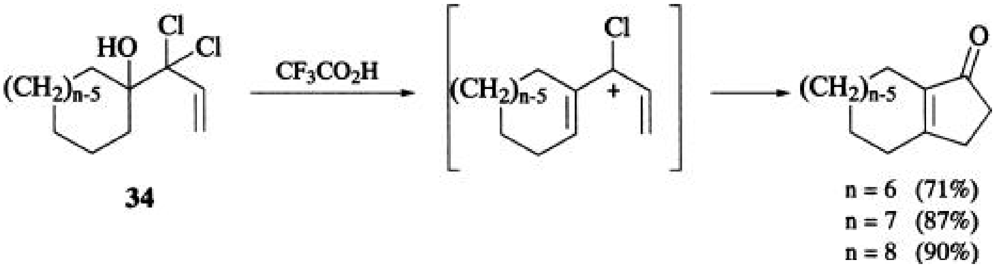


(30)

3.4. Solvolytic Generation of Divinyl Ketones or Equivalents

3.4.1.1. *From gem-Dichlorohomoallyl Alcohols*

The structural diversity of divinyl ketone equivalents as precursors to cyclopentenones found in this class is remarkable. While this diversity lends breadth to the scope of the ring forming process, the reaction conditions required to unveil the precursor are often harshly acidic. Such is the case in the transformation of dichloro homoallylic alcohols **34**. These compounds (available from addition of 1,1-dichloroallyllithium to ketones) undergo solvolysis in neat trifluoroacetic acid to afford cyclopentenones in good yield (Eq. 31). (109, 110) The reactions likely proceed by initial dehydration to the divinyl dichloride followed by ionization to a 3-chloropentadienylic cation.

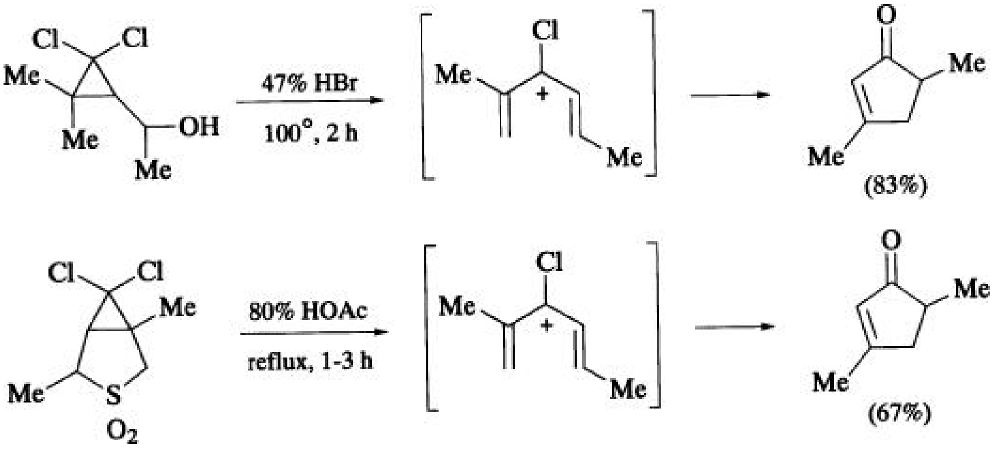


34

(31)

3.4.1.2. From gem-Dichlorocyclopropylmethanols

The same manifold of intermediates can be accessed from dichlorocyclopropanes in two different ways (Eq. 32).



(32)

The first involves solvolysis of the dichlorocyclopropyl carbinols. Heating the carbinols in 47% hydrobromic acid affords cyclopentenones in good yields. The cyclopropylcarbinyl cation rearranges with loss of a proton to a divinyl dichloride as in the previous reaction. Because of the ready availability of the precursors from dichlorocyclopropanation of allylic alcohols, this procedure is best suited for the preparation of simple cyclopentenones. (110, 111) In the second procedure, the dichlorocarbene/3-sulfolene adduct suffers extrusion of sulfur dioxide to form the divinyl dichloride which (under the solvolysis conditions) proceeds analogously to cyclopentenones. (112)

3.4.1.3. Rearrangement of Vinylallene Oxides

Peracid epoxidation of vinylallenes bearing allenic substituents results in the formation of cyclopentenones (Eq. 33). If no allenic substituents are present, epoxidation occurs on the vinyl group, leading to a stable oxirane. The details of this intriguing process are still unknown, but the intermediacy of a vinylallene oxide has gained support recently. (59) Rearrangement of the allene oxide may proceed via a 2-oxidopentadienyl cation or a cyclobutanone.

The procedure is applicable to both simple and fused cyclopentenones with various substitution patterns using either peracids or singlet oxygen. (113-122)

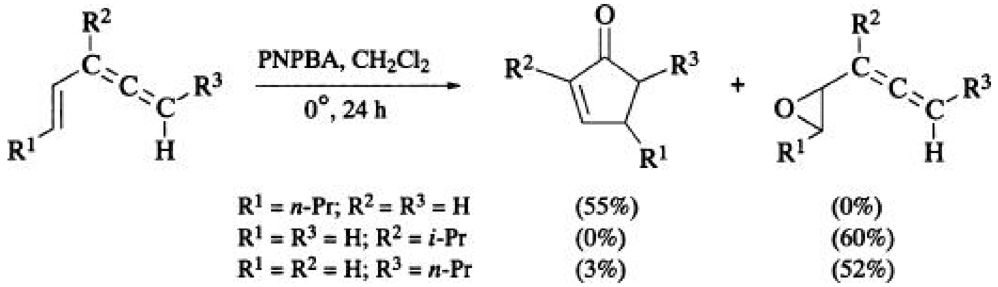
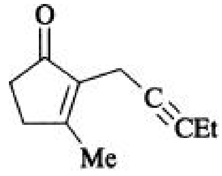
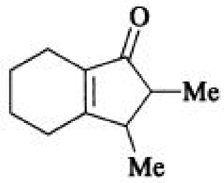


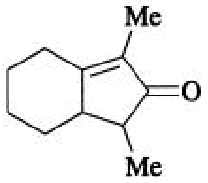
Figure 6.



(70%)

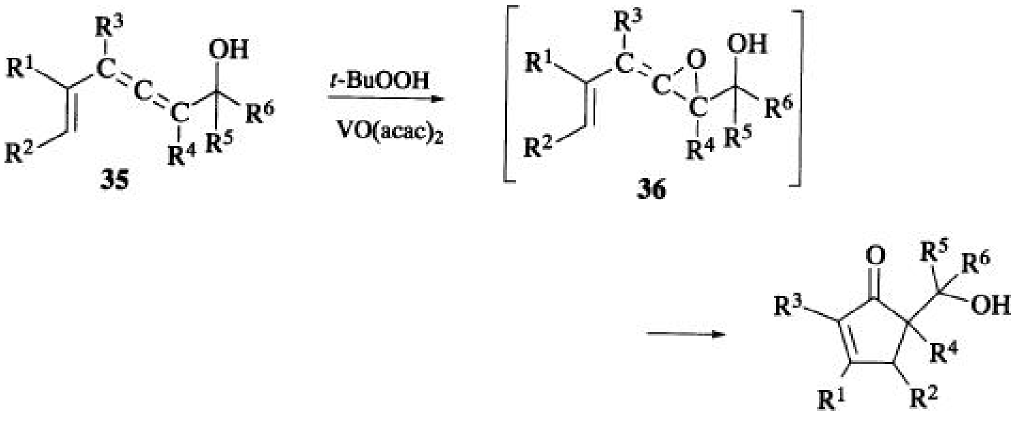


(50%)



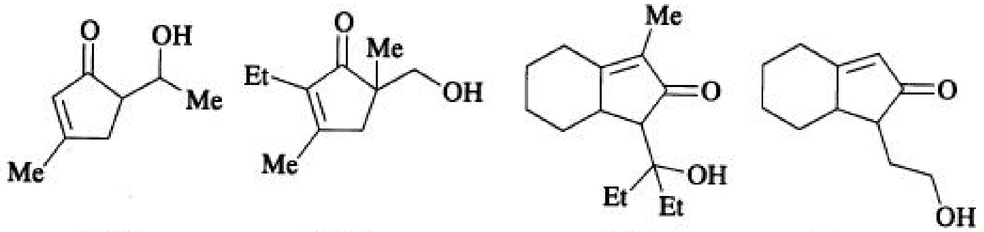
(50%)

The unproductive oxidation of the vinyl double bond can be suppressed by taking advantage of hydroxy-directed epoxidation of allylic and homoallylic alcohols. Attachment of allylic or homoallylic type hydroxy groups at either position of the allene unit is effective. (123-126) At the 1 position, for example, **35** (Eq. 34),



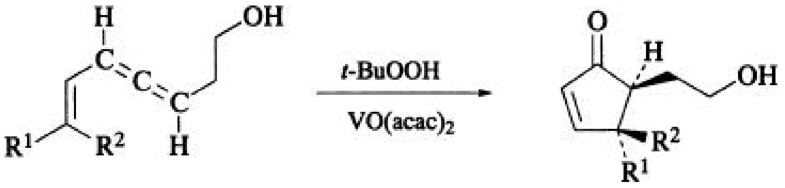
35 **36**

(34)



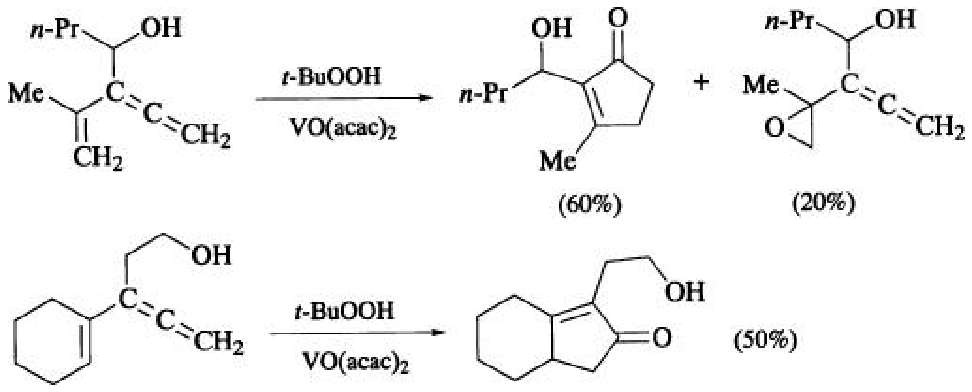
(55%) (63%) (45%) (40-70%)

primary, secondary, and tertiary allylic alcohols and primary homoallylic alcohols have been examined. Presumably, the cyclopentenones are formed via the intermediacy of vinylallene oxide **36**. Finally, an important stereocontrol feature has been noted in the homoallylic alcohols (Eq. 35) that is consistent with either a concerted or zwitterionic mechanism.



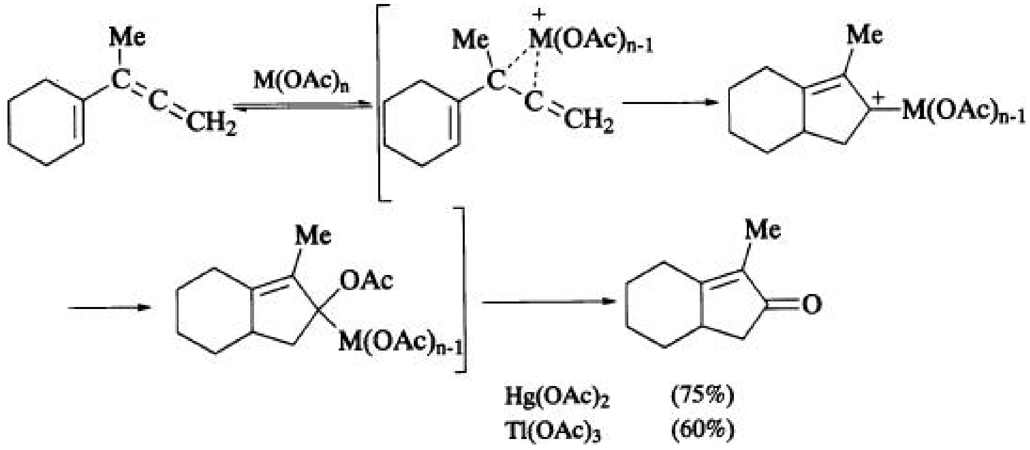
(35)

Placement of the epoxidation-directing substituent at the 3 position also leads to cyclopentenones, but the regioselectivity of epoxidation is dependent on the location of and substitution at the hydroxy-bearing group. (124, 126) With allylic alcohols, secondary hydroxy groups lead primarily to cyclopentenones, while tertiary hydroxy groups lead exclusively to allenyl epoxides. With homoallylic alcohols, cyclopentenones are the major products independent of the substitution pattern (Eq. 36).



(36)

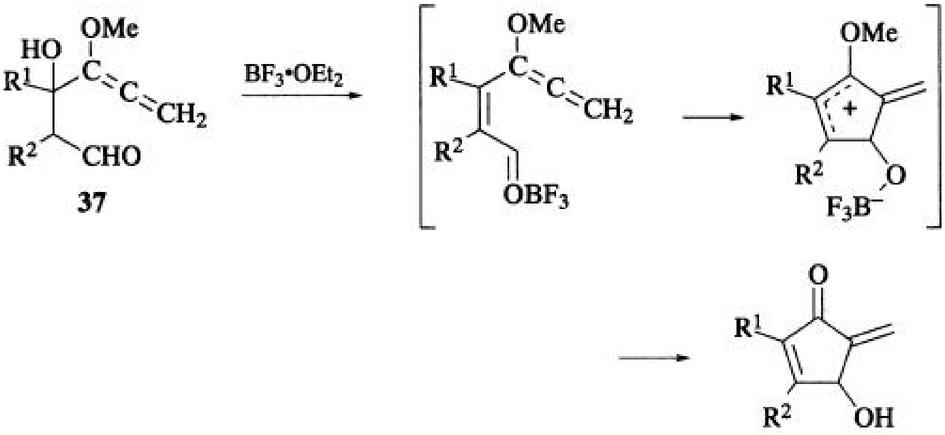
Vinylallenes can also be converted to cyclopentenones by solvometallation in the presence of mercury(II) acetate or thallium(III) acetate (Eq. 37). Electrophilic



(37)

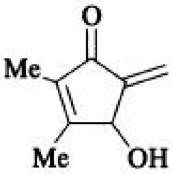
activation of allenes by these metal salts is a well-precedented Markownikoff process. In this case a spontaneous demetallation takes place to afford the cyclopentenone and the nascent metal. The yields are improved in general by the use of acetoxymercuration compared to acetoxythallation. (127, 128)

Although mechanistically unrelated to the foregoing vinylallene processes, the solvolysis of methyoxyallenyl alcohol **37** in the presence of boron trifluoride etherate constitutes an efficient construction of α-methylenecyclopentenones (Eq. 38). (129-131) This transformation has been generalized to incorporate different

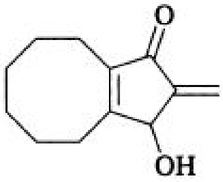


37

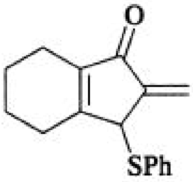
(38)



(68%)



(80%)



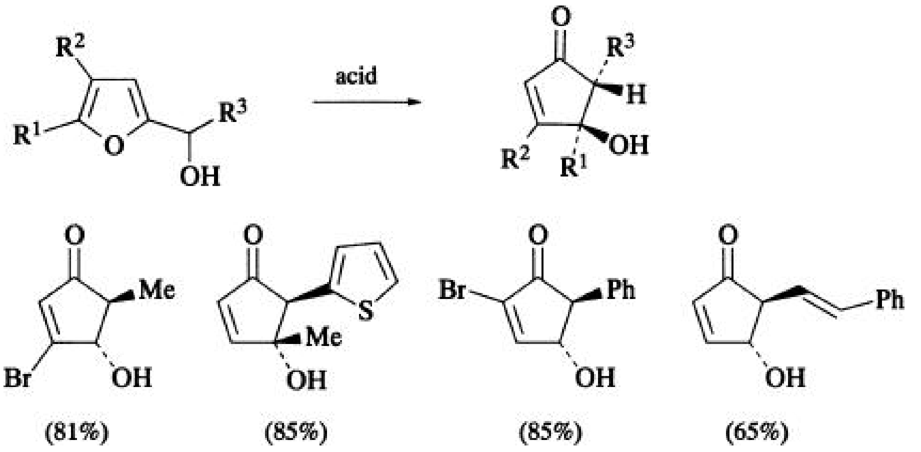
(82%)

functional groups in the product and is ideally suited for the synthesis of α -methylenecyclopentanoid natural products. The electrocyclic process is formulated as a closure of a 1-oxypentadienylic cation closely related to the solvolysis of 2-furyl carbinols described in the next section.

3.4.1.4. From 2-Furyl Carbinols

The acid-catalyzed rearrangement of 2-furyl carbinols constitutes a versatile, albeit modest synthesis of 4-hydroxy-2-cyclopentenones (Eq. 39). (132-139) An important advantage of this synthesis is the ready availability of the precursors from a Grignard reaction of furfural. The choice of acid catalyst for the reaction is guided by the substitution on the furan ring. For bromo- or unsubstituted furans the reaction is sluggish, and sulfuric acid is used. For alkyl-substituted furans, zinc chloride is recommended.

Mechanistically, the reaction is intriguing as it corresponds to the in situ formation of a conjugated dienone rather than a cross-conjugated divinyl ketone. Thus, cyclization in a Nazarov sense (as a 1,4-dihydroxypentadienylic cation)



(39)

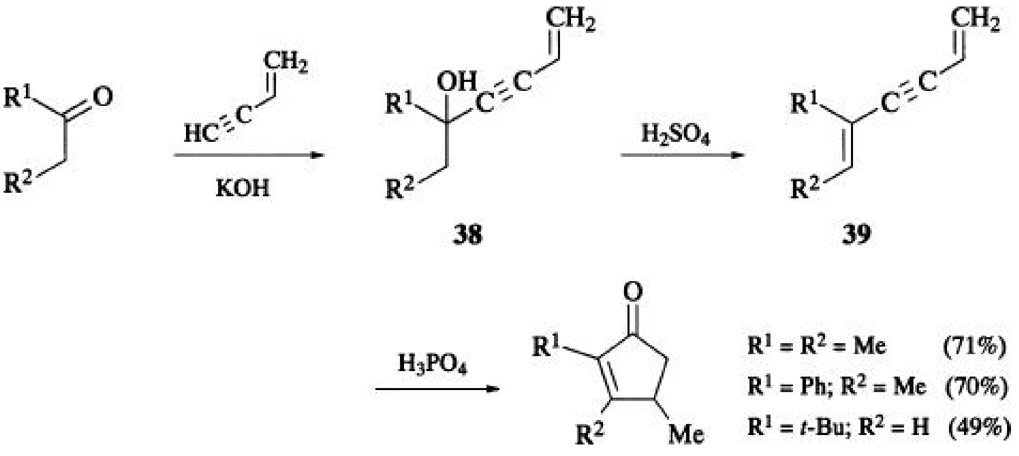
leads to a 4-hydroxy-2-cyclopentenone. An important consequence of the electrocyclization is the *trans* relationship of the 4-hydroxy group and the 5 substituent.

3.5. Acetylene-Containing Precursors

The acid-catalyzed hydration of acetylenes to ketones provides general access to carbonyl compounds from hydrocarbon precursors. The functionality needed to provide the additional double bonds to produce the equivalent of divinyl ketones can be derived from alkenes, alcohols, amines, or acetals.

3.5.1.1. Dienynes

The simplest progenitors of divinyl ketones are dienynes. (13-15, 22-25, 31) These compounds are easily prepared by addition of vinylacetylenes to ketones followed by dehydration (usually in a Saytzeff sense, Eq. 40). In certain cases,



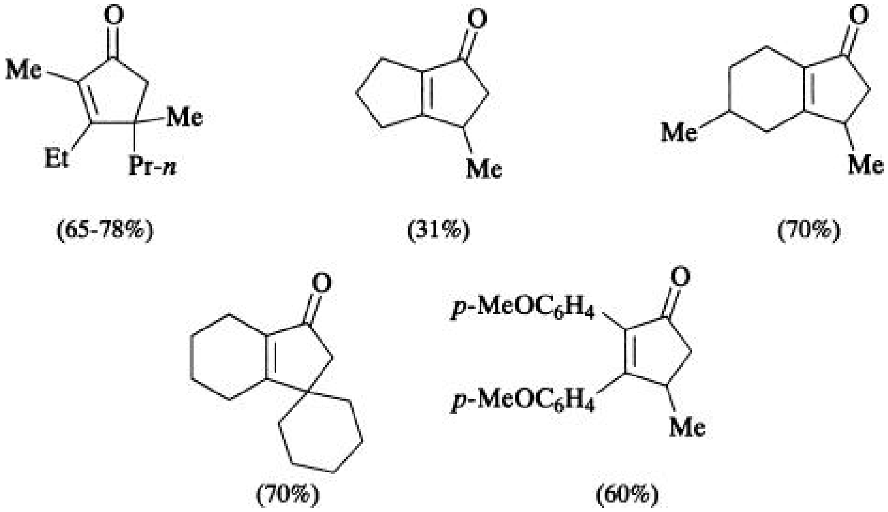
(40)

the vinylacetylenic alcohol **38** is directly employed, since the dehydration, hydration, and cyclization are all acid-catalyzed steps. (11, 31, 33, 34, 140)

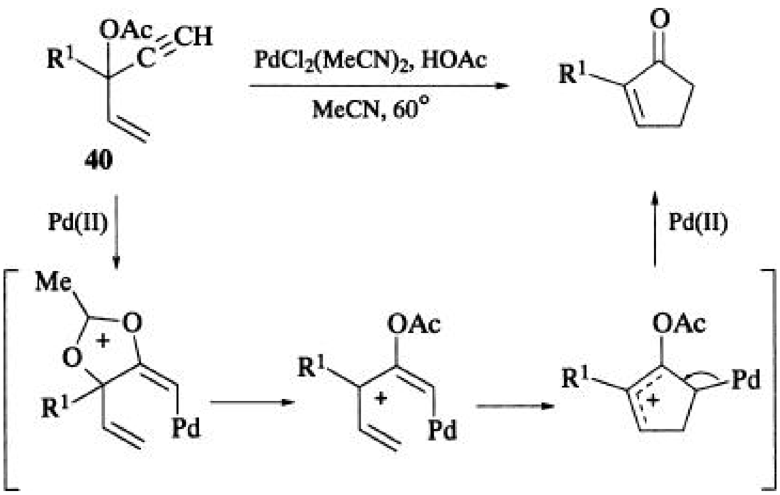
The preparation allows for general access to both cyclic and acyclic dienynes **39** at various levels of substitution. The conditions required for transformation to cyclopentenones are rather harsh (concentrated phosphoric or hydrochloric acid, 50–80°) since both hydration of the acetylene and cyclization must take place.

The majority of examples of this process employ vinylacetylene itself, which affords 1,2-disubstituted 4-methyl-2-cyclopentenones. α -Branched ketones afford 3-methyl-4,4-disubstituted 2-cyclopentenones. (24, 25) If cyclic ketones are employed as precursors, the overall process constitutes a cyclopentenone annulation. (22, 26, 31, 141)

Figure 7.



Although the enynols **38** are readily accessible and can be transformed into cyclopentenones, their molecular connectivity is not optimal since an array of six atoms is required to produce the requisite divinyl ketone equivalent that minimally needs only five atoms. This concept is illustrated by the rearrangement of the isomeric enynol acetate **40**. The cyclization is promoted by a palladium(II) catalyst in warm acetonitrile by the mechanistically intriguing process outlined in Eq. 41. (142) The reaction bears a resemblance to the silicon-directed Nazarov cyclization

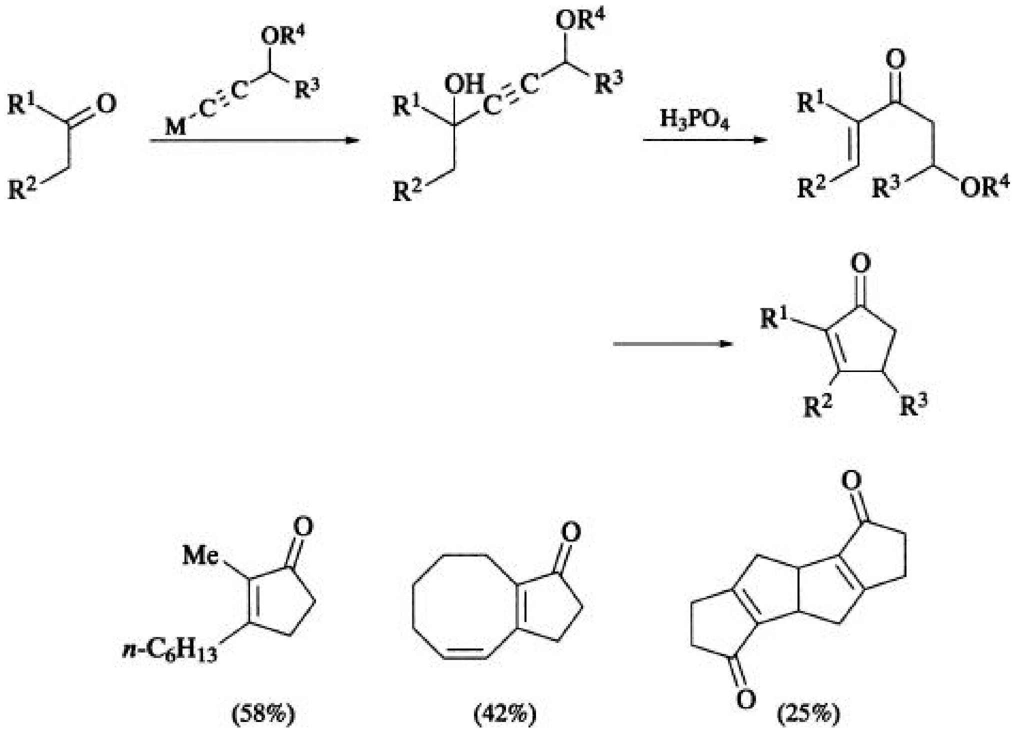


(41)

in the ejection of the palladium(II) electrofuge. Both secondary and tertiary acetates can be employed, but substitution has been examined only at the a -vinyl position.

3.5.1.2. Propargylic Alcohols and Derivatives

A variety of other structural modifications that involve replacement of the terminal double bond with an oxidized carbon group (alcohol, amine, acetal) are also amenable to cyclization. The most common variation on this theme involves the acid-catalyzed transformation of ynediols available from the addition of propargylic alcohols and ethers to ketones (Eq. 42). (143-154) The advantages of this method are that the conditions are milder



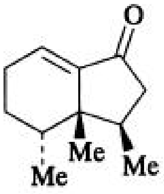
(42)

than those for dienynes, rarely requiring heating (most likely proceeding via a Rupe rearrangement), and the substitution at C-4 is easily varied and can be hydrogen. For many years this reaction constituted the cyclopentanone annulation method of choice. Acyclic and monocyclic substrates containing 5-, 6-, 7-, 8-, and 12-membered rings are compatible. Double annulations are also possible for the rapid construction of polyquinanes. The analogous transformation of acetylenic amino alcohols for cyclopentenone annulation proceeds albeit in lower yields. (155)

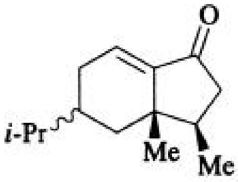
If the higher oxidation state propargyl acetals are employed, an additional double bond is incorporated in the product. (156) Unfortunately, the yields from this variant are generally low and the position of the double bond is not controllable.

Respectable levels of relative asymmetric induction (torquoselectivity) can be obtained in this variant. (147) The major diastereomer obtained from conrotatory closure depends on the position and nature of the substituent. If the substituent is vicinal to the newly forming stereocenter as in **41** the extent of 1,2-induction is very high. However, if the substituent is more remote, as in **42** and **43**, the extent of stereoselection is dependent on the size of the substituent, with the selectivity decreasing from isopropyl to methoxycarbonyl.

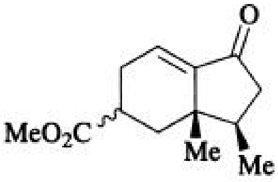
Figure 8.



41 (60%)



42 (60%)
cis/trans 87/13



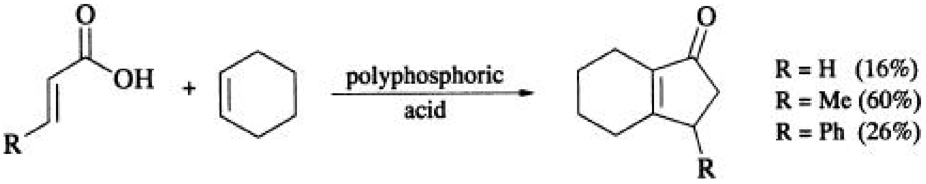
43 (60%)
cis/trans 60/40

3.5.1.3. Divinyl Ketones from Coupling

In this category the precursors of the cyclopentenone are the most structurally remote because the carbon skeleton of the divinyl ketone is constructed during the operation. In all other variants, the carbon skeleton is assembled first and then, through functional group manipulations, the divinyl ketone equivalent is revealed under conditions that induce cyclization. With one exception, the carbon–carbon bond forming reactions are acylations of alkenes or acetylenes.

3.5.2.1. From α , β -Unsaturated Acids

α , β -Unsaturated acids or anhydrides undergo aliphatic Friedel-Crafts reaction with cycloalkenes to ultimately afford fused cyclopentenones (Eq. 43). The conditions for generation of the unsaturated acylium

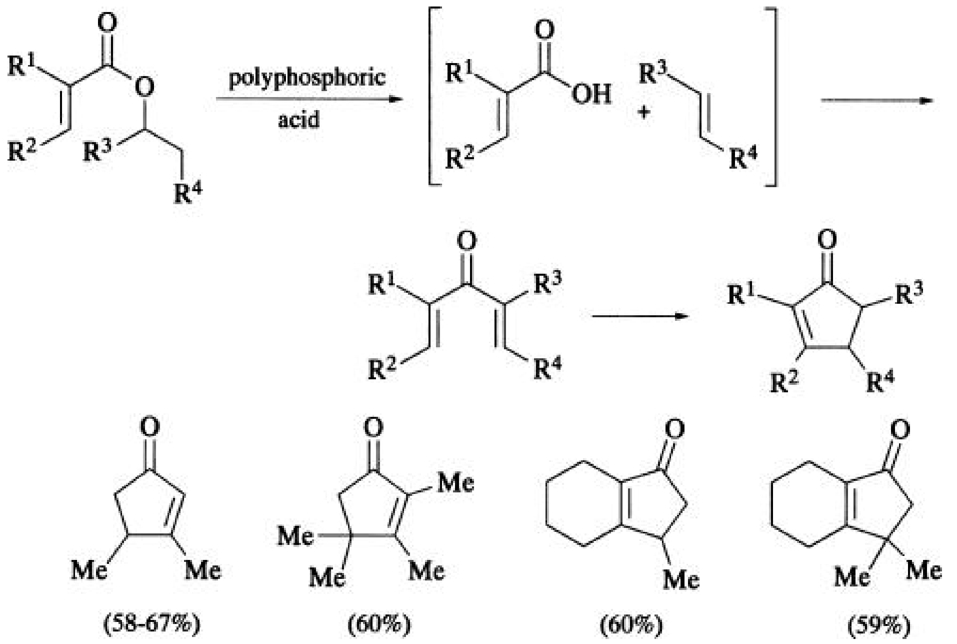


(43)

ions are sufficiently acidic (polyphosphoric acid, 40–60°) to effect the Nazarov cyclization of the intermediate divinyl ketones. Yields are in general modest.

3.5.2.2. From α , β -Unsaturated Esters

Treatment of α, β -unsaturated esters with polyphosphoric acid also produces cyclopentenones. This variant is an alternative entry to the unsaturated acylium ion/alkene mixture that produces divinyl ketones by Friedel-Crafts acylation. The action of hot polyphosphoric acid on olefinic esters causes ionization of the alkyl-oxygen bond, leading to a mixture of unsaturated acid and alkene (Eq. 44). Although the yields are better by this in situ



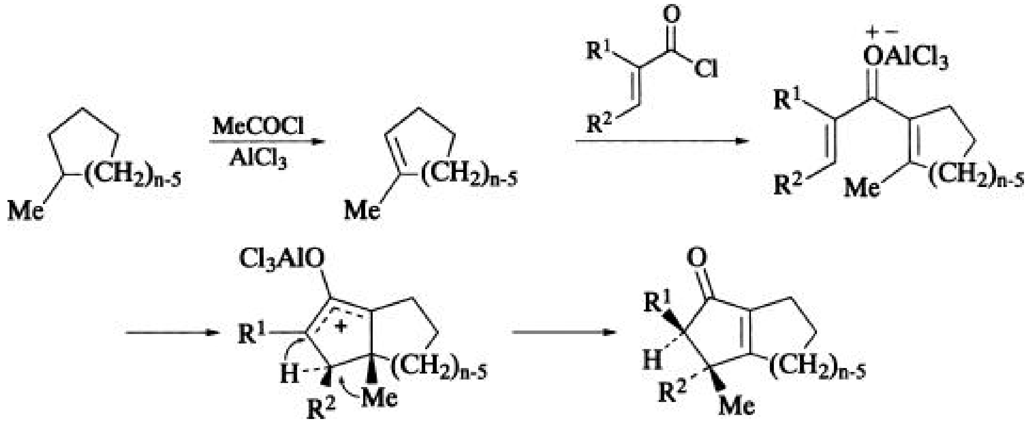
(44)

generation protocol, a disadvantage of this approach is the potential for generation of different alkenes in the cleavage reaction. Another problem (intrinsic to all acylations) is the regiochemical ambiguity in the reaction of unsymmetrically substituted alkenes (R^1 ¹ R^2). The ease of preparation of the starting esters allows for ready alteration of the substitution pattern in the cyclopentenone.

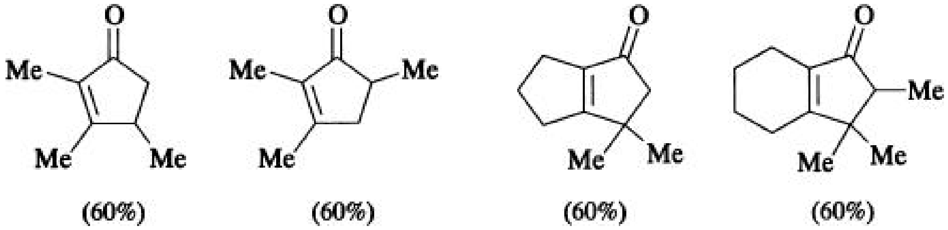
3.5.2.3. From α , β -Unsaturated Acid Chlorides

The most commonly employed precursors of unsaturated acylium ions are acid chlorides and bromides. The acylation of alkenes with these reagents constitutes a general synthesis of divinyl ketones which, under the conditions of acylation, suffer Nazarov cyclization to cyclopentenones. (157) As with the other carboxy precursors, the regioselectivity of electrophilic attack is ambiguous unless the alkene is either symmetrical or strongly biased toward Markownikoff addition. Both acid chlorides and bromides have been employed together with both cyclic and acyclic alkenes. Aluminum trichloride is the preferred Lewis acid promoter. Occasionally, the intermediate divinyl ketone or a β -chloroenone can be isolated.

Isoalkanes have also been employed as precursors of the alkenes in combination with alkenoyl chlorides (Eq. 45). (157a) The isoalkanes are oxidized to alkenes by hydride transfer to acetyl chloride/aluminum chloride or copper(II) sulfate in nitromethane. The isoalkanes (methylcyclopentane, methylcyclohexane, and 2-methylbutane) afford trisubstituted alkenes which undergo in situ

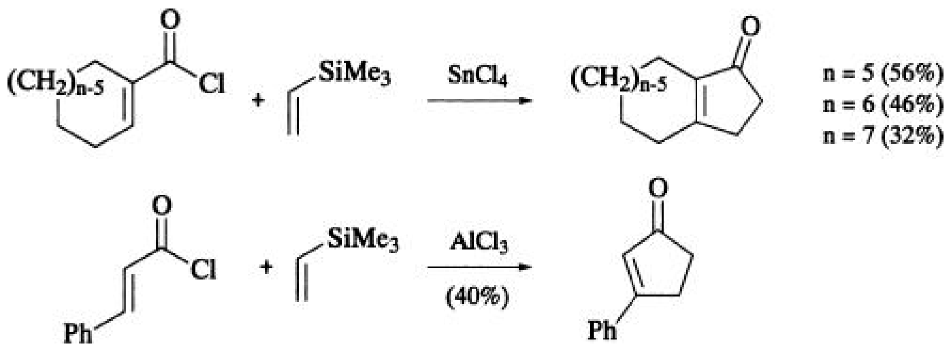


(45)



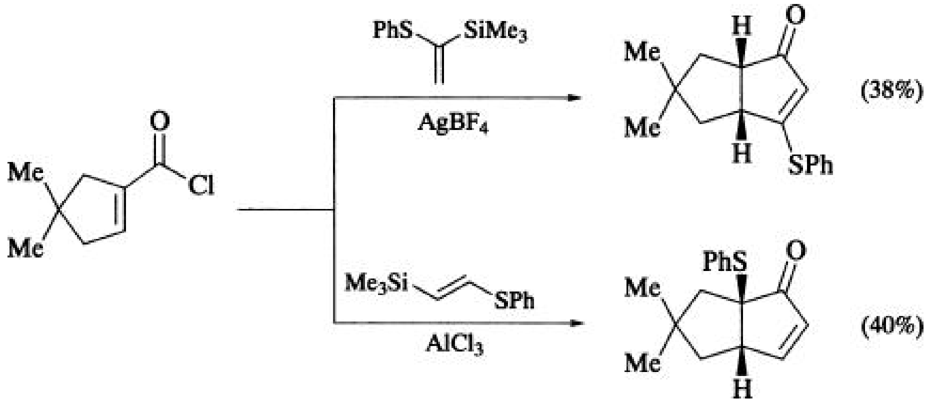
acylation/Nazarov cyclization as described above. Labeling studies have revealed the involvement of hydride and alkyl migrations in the formation of the cyclopentenones.

A significant improvement in the utility of this approach is the employment of vinylsilanes for the preparation of the intermediate divinyl ketones. Owing to the ability of the silicon moiety to direct the site of electrophilic substitution, the problem of regiochemical ambiguity is resolved. Vinylsilane reagents have been used in two different modes. The first employs vinyltrimethylsilane itself as an ethylene equivalent in combination with olefinic acid chlorides. (158, 159) This is used primarily for the annulation of the cyclopentenone ring. Tin tetrachloride is the reagent of choice to promote both electrophilic substitution and the Nazarov cyclization. The double-bond position is thermodynamically controlled. Substituted acryloyl chlorides also react with vinyltrimethylsilane to afford simple cyclopentenones. (160) For this variant, aluminum chloride is the preferred reagent (Eq. 46).



(46)

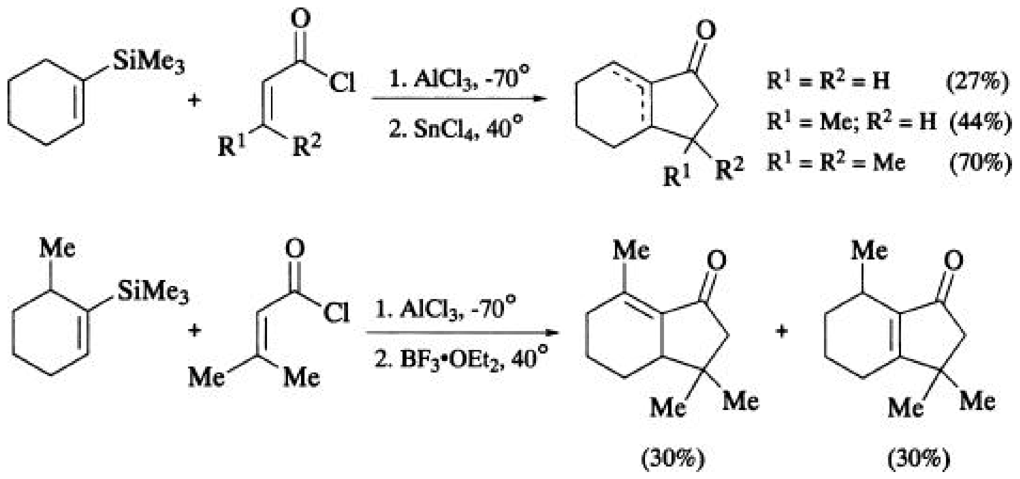
1- and 2-Phenylthio-substituted vinylsilanes are also useful reagents for cyclopentenone annulation. (161-163) The products of reaction with these reagents are very different (Eq. 47). In annulation reactions with a cyclopentenoyl chloride,



(47)

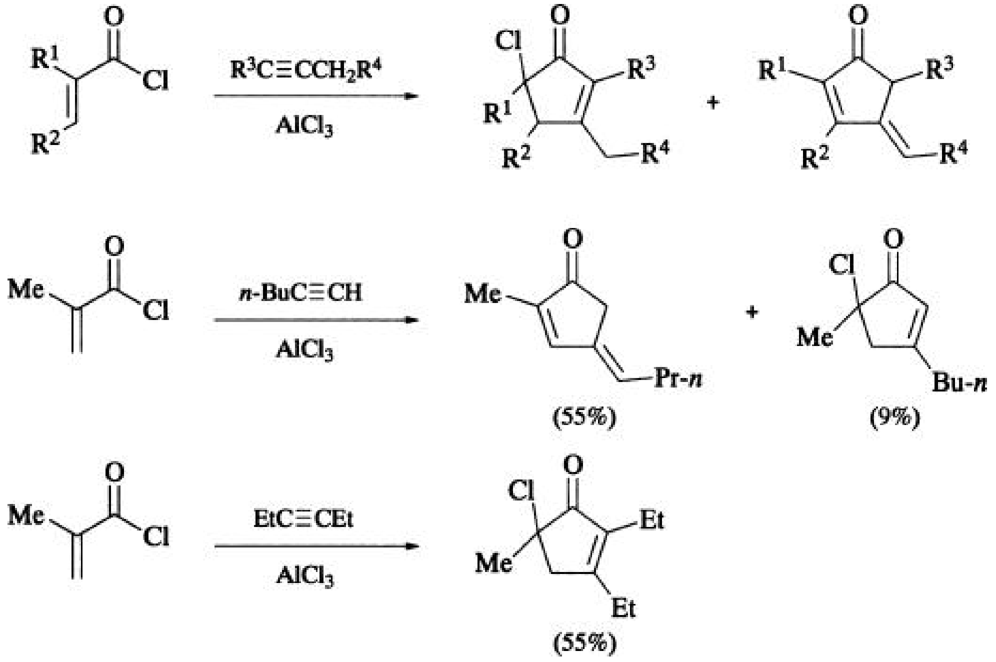
1-phenylthiovinyltrimethylsilane affords 3-phenylthio-2-cyclopentenones while the 2-phenylthiovinyltrimethylsilane affords 5-phenylthio-2-cyclopentenones. In both cases the yields are modest.

The second application of vinylsilanes in the Nazarov cyclization uses substituted acryloyl chlorides in combination with cyclic vinylsilanes. (67, 68) In general the vinylsilanes are obtained by silylation of the vinyllithium reagents generated from the corresponding hydrazones. In this modification the two steps are promoted by different Lewis acids: aluminum trichloride for the acylation and tin tetrachloride or boron trifluoride etherate for the Nazarov cyclization. The yield of the reaction is dependent on the degree of substitution of the alkenoyl chloride in the following order: β , β -disubstituted > β -monosubstituted > unsubstituted. With β , β -disubstituted acryloyl chlorides, the position of the cyclopentenone double bond is not well controlled (Eq. 48).



(48)

The acylation of acetylenes with alkenoyl chlorides constitutes an alternative construction of cyclopentenones in a higher oxidation state. This reaction is most likely not mechanistically related to the Nazarov cyclization, rather involving electrophilic attack of the vinyl cation on the enone double bond. The major products are 5-chloro-2-cyclopentenones and 3-alkylidene-2-cyclopentenones along with chlorinated divinyl ketones. The ratio of chloro- to alkylidenecyclopentenones is dependent on the type of alkyne employed as illustrated for hexyne isomers: terminal alkynes afford mostly alkylidenecyclopentenones while internal alkynes (and acetylene itself) afford mostly chlorocyclopentenones (Eq. 49). (164-167)



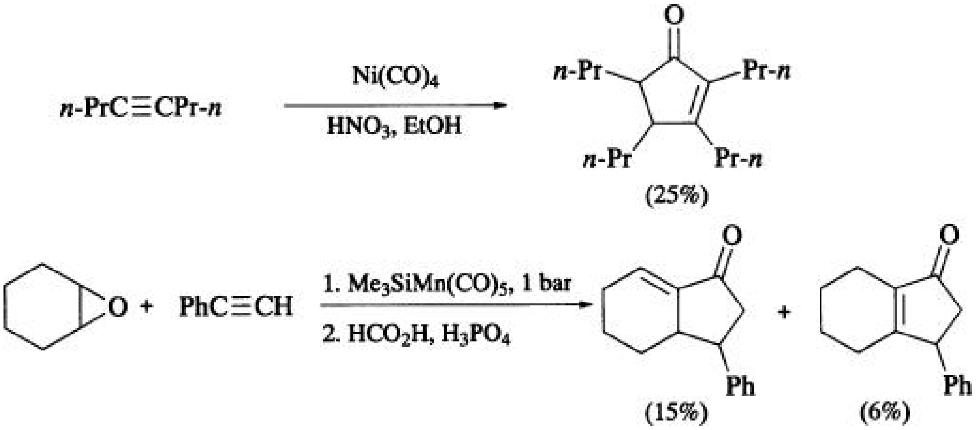
(49)

3.6. Miscellaneous Couplings

The construction of cyclopentenones from metal carbonyl compounds is a powerful technology, albeit unrelated to the Nazarov cyclization. There are however, two organometallic carbonylation reactions that most likely involve the formation of divinyl ketones which cyclize under the reaction conditions to afford cyclopentenones (Eq. 50). (168, 169)

4. Synthetic Utility

Several variants of the Nazarov cyclization have been employed in synthesis endeavors. For example, syntheses of simple cyclopentanoids such as *cis*-jasmone, (111) prostaglandin analogs (135, 136, 170) and (±)-valleranal, (122) (±)-methyleneomycin B, (130) and (±)-xanthocin (131) feature the Nazarov cyclization as a key step. More recently



(50)

the Nazarov cyclization has been used in the synthesis of polyquinane natural products such as (±)-hirsutene, (163) (±)-modhephene, (171, 172) (±)-silphinene, (100, 148) (±)-pentalenene, (100a) (±)- D $^{9(12)}$-capnellene, (95) and (±)-cedrene. (173) The synthesis of (±)-D$^{9(12)}$-capnellene is noteworthy for the use of the silicon-directed Nazarov cyclization in an iterative fashion. The synthesis of yuehchukene alkaloid analogs has also employed a Nazarov cyclization as a key step. (173a)

The Nazarov cyclization employing propargyl alcohols has been successfully applied to the synthesis of (±)-strigol, (145) (±)-nor-sterepolide, (150) (±)-nookatone, (147) (±)-muscone, (152, 174) and (±)-muscopyridine. (147) Industrially, an aromatic Nazarov cyclization is used in the synthesis of (+)-indacrinone. (78)

A Nazarov-type cyclization has been postulated in the biosynthetic pathways for *cis*-jasmonic acid (175, 176) and marine-derived prostanoids such as preclavulone A. (177, 178)

5. Experimental Conditions

The diversity of substrates that are employed in the Nazarov cyclization and their differing propensity to be transformed into the divinyl ketone equivalents preclude generalizations about the reaction conditions. Since the cyclization of divinyl ketones requires the formation of a 3-oxypentadienylic cation, protic acids or Lewis acids are usually involved. The classical reagent for Nazarov cyclizations is polyphosphoric acid, usually in formic acid solution, or sulfuric acid in methanol. Modern variants employ Lewis acids such as tin tetrachloride, boron trifluoride etherate, aluminum trichloride, or ferric chloride in chlorocarbon solvents

6. Experimental Procedures

The procedures described below are chosen to be representative of each of the important structural classes of precursors for cyclopentenones. The generic structural class of precursor is provided parenthetically after the compound name.

6.1.1.1. 3,4,4-Trimethyl-5-phenyl-2-cyclopentenone (Cyclization of an Allyl Vinyl Ketone) (24)

2-Methyl-3-phenyl-2,6-heptadien-4-one (12 g, 0.60 mol) was slowly added with stirring to 15 g of conc. phosphoric acid (sp. gr. 1.82). The mixture evolved enough heat to reach a temperature of 85° and quickly became homogeneous. After being stirred at 70° for 40 minutes, the reaction mixture was diluted with water and then extracted with diethyl ether. The organic extracts were washed with sodium bicarbonate solution, dried over magnesium sulfate, and then concentrated. The residue was vacuum distilled to afford 10 g of the product (83%); bp 129–130° (2 torr); n_D^{20} 1.5520; d_4^{20} 1.044. Anal. Calcd. for $C_{14}H_{16}O$: C, 83.92; H, 7.99. Found: C, 83.69; H, 8.15. The ketone solidified after distillation and was recrystallized from 80% ethanol; mp 49°. The semicarbazone of this ketone was also prepared; mp 221.5°.

6.1.1.2. cis-Tricyclo[6.3.0.0^{3,7}]undec-1(8)-en-2-one (Cyclization of a Divinyl Ketone) (71)

1,1¢-Dicyclopentenyl ketone (19 g, 0.12 mol) was added with good stirring to hot (100°) polyphosphoric acid (100 g) under nitrogen. The colorless solution immediately turned dark brown. The reaction mixture was stirred for 30 minutes at 100°. After this time, the reaction solution was cooled in an ice bath, and ice (100 g) was added immediately to the hot acid. The mixture was stirred for 5 minutes. A dark precipitate formed during the addition of ice, but dissolved on the addition of diethyl ether. Standard extractive workup with ether gave a brown oil (19 g) which was distilled carefully to give 11.9 g (62% yield) of a the tricyclic product of greater than 95% isomeric purity by gas chromatography (OV-225) as a colorless oil; bp 60–63° (0.05 torr); UV nm max (ε) 244 (3700), 308 (72); IR (Nujol) 1690, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$, 270 MHz) δ multiplets centered at ca. 3.2 (1H), 3.1 (1H), 2.5 (2H), 2.4 (4H), 1.9 (1H), 1.6 (4H), and 1.3 (1H). A 2,4-dinitrophenylhydrazone of the product was also prepared, mp 201–202° (chloroform/ethanol).

6.1.1.3. cis,trans-1,3,4,5,6,7,8,8a-Octahydroazulen-1-one (Silicon-Directed Cyclization) (85)

Anhydrous iron trichloride (345 mg, 2.13 mmol) was added in one portion to a cold (–5°) solution of (*E*)-1-(1-cycloheptenyl)-3-trimethylsilyl-2-propen-1-one (450 mg, 2.02 mmol) in 25 mL of dichloromethane. The mixture was stirred at

–5° for 50 minutes by which time the starting material had been consumed. Water (20 mL) was added, the mixture was diluted with dichloromethane (10 mL), and the organic layer was removed. The aqueous phase was extracted with dichloromethane (2 × 30 mL) and the individual organic extracts were washed with saturated aqueous ammonium chloride solution and brine. The combined organic extracts were dried (K_2CO_3) and concentrated. The residue was purified by flash column chromatography on silica gel (eluting with hexaneethyl acetate 4:1) followed by distillation, bp 110° (0.01 torr) to afford 225 mg (74%) of the azulenone. GC analysis revealed the product to be an 85/15 mixture of *cis* and *trans* isomers; IR ($CHCl_3$) 3010, 2940, 1705 (C = O), 1580 (C =C) cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 7.85 (dd, J = 5.0, 2.0 Hz, 1H), 6.40 (dd, J = 5.0, 1.5 Hz, 1H), 3.55–3.25 (m, 1H), 2.92–2.62 (m, 1H), 2.48–1.38 (br m, 10H); mass spectrum m/z (rel. intensity) 150 (68), 135 (28), 108 (65), 107 (78), 95 (100), 94 (30), 93 (32), 83 (35), 79 (71), 77 (36), 68 (32), 67 (40), 66 (32), 53 (42). Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.85, H, 9.50.

6.1.1.4. (4ab,4ba,9aa)-1,2,3,4,4a,4b,5,6,7,9a-Decahydro-1H-fluoren-9-one (Silicon-Directed Cyclization of an Allylsilane) (89)

To a cold, (–50°) stirred mixture of anhydrous iron trichloride (170 mg, 1.05 mmol) in dry dichloromethane (40 mL, 0.02 M) was added dropwise a solution of (1-cyclohexenyl) (6-trimethylsilyl-1-cyclohexenyl) ketone (262 mg, 1.00 mmol) in 10 mL of dichloromethane. The reddish-brown mixture was allowed to stir 1 minute and then quenched by the addition of brine (50 mL) and diluted with diethyl ether (50 mL). The water layer was separated, extracted with diethyl ether (2 × 50 mL) and the combined diethyl ether extracts were washed with water (75 mL) and brine (75 mL), and then dried ($MgSO_4$) and evaporated to afford 157 mg (79%) of the product as a clear and colorless oil; bp 85° (0.3 torr); mp 78.5–79.5° (pentane); R_f: 0.23 (hexane/EtOAc 19/1); IR (neat): 2921s, 2854s, 2813w, 1713s, 1653s, 1449s, 1415 m, 1363w, 1349w, 1293 m, 1244 m, 1232w, 1222w, 1208 m, 1196w, 1173w, 1144w cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.64 (d, J = 2.6 Hz, 1H), 2.35–2.19 (m, 1H), 2.19–1.61 (m, 6H), 1.70–1.91 (m, 3H), 1.55–1.37 (m, 1H), 1.30–0.84 (m, 6H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 204.7, 141.0, 131.5, 54.9, 48.1, 42.4, 30.3, 26.5, 25.9, 25.5, 25.1, 21.4. MS (70 eV) m/z (rel. intensity) 190 (M^+, 82), 163 (11), 162 (84), 161 (32), 149 (10), 148 (14), 147 (18), 134 (11), 133 (19), 109 (15), 108 (100), 98 (20), 94 (50), 81 (24), 80 (55), 79 (39). Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.11; H, 9.54.

6.1.1.5. Bicyclo[10.3.0]pentadec-1(12)-en-13-one (Solvolysis of a Dichloro Homoallyl Alcohol) (109)

1-(1,1-Dichloro-2-propenyl)cyclodecanol (105 g, 0.36 mmol) was added in one portion to trifluoroacetic acid (1.3 mL) at room temperature. The dark red solution was stirred vigorously for 1.5 hours and then was diluted with diethyl ether (10 mL) and neutralized with aqueous sodium bicarbonate solution. The mixture was extracted with diethyl ether (4 × 20 mL) and the combined organic extracts were dried (Na_2SO_4) and concentrated in vacuo to give an oil, which was purified by preparative TLC (silica gel, dichloromethane-diethyl ether, 10/1) to afford 71 mg (90%) of the product; ^{1}H NMR ($CDCl_3$ 60 MHz) δ 2.6–1.9 (m, 8H), 1.9–0.9 (m, 16H); IR (neat) 1690, 1634 cm^{-1}; mass spectrum *m/z* (rel. intensity) 220 (M^+, 65), 177 (93), 149 (100), 110 (65).

6.1.1.6. 2-Pentyl-2-cyclopentenone (Epoxidation of a Vinylallene) (119)

4-Nitroperoxybenzoic acid (3.66 g, 0.02 mol) was added in small portions to a cold (0°), stirred solution of 3-pentyl-1,2,4-pentatriene (2.73 g, 0.02 mol) in dichloromethane (50 mL). After being stirred at 0° for 24 hours, the suspension was filtered and the filtrate was washed with 5% aqueous sodium hydroxide (3 × 20 mL) and water and was then dried ($MgSO_4$). The dichloromethane was evaporated and the residue was purified by silica gel chromatography (petroleum ether–ether, 20/1) to afford 2.42 g (80%) of the product; IR (neat) 3040, 1705, 1445, 1050, 1000 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.15 (m, 1H), 2.75–1.90 (m, 6H), 1.80–1.10 (m, 6H), 0.89 (t, 3H).

6.1.1.7. Methylenomycin B (Solvolysis of a Methoxyallenyl Vinyl Carbinol) (130)

Trifluoroacetic anhydride (2.3 mL, 16.3 mmol) was added dropwise over 15–30 minutes to a cold (–20°) solution of 2,3-dimethyl-3-hydroxy-4-[(methoxymethyl)oxy]-1,4,5-hexatriene (1.0 g, 5.4 mmol) containing 2,6-lutidine (3.1 mL, 27 mmol). After 5–10 minutes at –20°, the reaction was quenched by the addition of water (3 mL) and the product was extracted into diethyl ether. The ether layer was washed with water and brine and dried over magnesium sulfate. Filtration followed by evaporation of the solvent furnished a residue which was purified by column chromatography on silica gel to afford 490 mg (74%) of methylenomycin B as a pale yellow oil which crystallized in the freezer; mp 4°; IR (neat) 1690, 1660, 1625 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.02 (m, *J* = 1 Hz, 1H), 5.32 (m, *J* = 1.5 Hz, 1H), 3.05 (br s, 2H), 2.04 (m, *J* = 1.0 Hz, 3H), 1.78 (m, *J* = 1.0 Hz, 3H); ^{13}C NMR (C_6D_6, 75 MHz) δ 194.79, 162.30, 142.35, 138.18, 114.11, 36.59, 15.90, 8.28; mass spectrum *m/z* (rel. intensity) 122, 107, 93, 86, 84, 79.

6.1.1.8. 3a-Methyl-2,3,3a,4,5,6-hexahydro-(1H)-inden-1-one (Cyclization of a Propargylic Diol) (147)

n-Butyllithium solution in hexane (2.0 M, 15.8 mL, 32 mmol) was added to a cold (–78°) solution of propargyl alcohol (0.85 g, 15.1 mmol) in THF (40 mL). After being stirred at –78° for 3 hours a solution of 2-methylcyclohexanone (1.12 g, 10.0 mmol) in THF (10 mL) was added and the solution was allowed to stir at –78° for 1 hour and then at room temperature for 0.5 hour. After aqueous workup, the crude oil was purified by silica gel column chromatography to afford the adduct (1.48 g, 88% yield) as a 3:2 mixture of diastereomers. The mixture was used for the subsequent cyclization.

Concentrated sulfuric acid (1.5 mL, 28 mmol) was added dropwise at 0° over 15 minutes to a solution of the adducts (162 mg, 0.96 mmol) in methanol (1.5 mL). After being stirred at 0° for 1.5 hours the reaction was diluted with diethyl ether (15 mL) and neutralized with aqueous sodium hydrogen carbonate solution. Extractive workup afforded a crude oil that was purified by preparative TLC (dichloromethane) to afford 101 mg (70%) of the product: bp 78–80° (0.04 torr); IR (neat) 1716, 1646 cm^{-1}; ^{1}H NMR (CCl_4, 90 MHz) δ 6.37 (t, *J* = 3.6 Hz, 1H), 2.5–1.2 (m, 10H), 1.08 (s, 3H); mass spectrum *m/z* (rel. intensity) 151 (M^+ + 1, 8), 150 (M^+, 42), 135 (32), 122 (33), 108 (75), 93 (88), 79 (100). Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.69; H, 9.33.

6.1.1.9. 1,2,3,4,5,6-Hexahydropentalen-1-one (Coupling of an α , β -Unsaturated Acid Chloride with Vinyltrimethylsilane) (68)

Tin tetrachloride (26.35 g, 101 mmol) was added dropwise to a cold (–30°) solution of cyclopentene-1-carbonyl chloride (12.00 g, 92 mmol) and vinyltrimethylsilane (10.13 g, 101 mmol) in dichloromethane (100 mL). The reaction mixture was allowed to stir at –30° for 1 hour and then warmed to 25° and stirred for 6 hours. The solution was poured onto water (100 mL) and extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with saturated aqueous sodium bicarbonate solution (100 mL), dried (Na_2SO_4), and evaporated in vacuo to afford 5.90 g (52.5%) of the product; bp 114–115° (13 torr); IR (neat) 2920, 2820, 1695, 1640, 1385, 1025 cm^{-1}; ^{1}H NMR (CCl_4, 60 MHz) δ 2.82–2.15 (m, 8H), 2.15–1.6 (m, 2H); mass spectrum *m/z* calcd. for $C_8H_{10}O$: 122.073, found 122.073.

7. Tabular Survey

The following tables contain examples of the Nazarov cyclization reaction in its various manifestations as defined in the preceding sections. The tables are arranged following the organizational format described in the Introduction. The table headings are self explanatory following the order of decreasing structural similarity to divinyl ketones. Within each structural subclass the listing of examples follows the order of increasing complexity from acyclic to monocyclic to polycyclic. Where established in the original articles, the configuration of the products is indicated. The literature survey includes articles appearing up to December 1991.

Since all of the carbon atoms for the final products appear in the starting material (with the exception of Tables V.A., V.C., and V.D.) the ordering of increasing carbon count for the starting materials and the products coincide. To further maintain this order, the carbon atoms of the silyl and tin substituents in the silicon- and tin-directed Nazarov cyclizations (Table II) are not counted. For the in situ construction of divinyl ketones (Tables V.A., V.C., and V.D.) the order follows increasing carbon count in the carboxylic acid derivative. For similar derivatives, the order of increasing complexity (acyclic, cyclic) followed by increasing carbon count (not including silyl substituents) of the olefinic or acetylenic component is observed.

The following abbreviations are used in the tables:

acac	acetylacetonate
Bn	benzyl
BOM	benzyloxymethyl
DME	1,2-dimethoxyethane
MCPBA	*m*-chloroperoxybenzoic acid
MOM	methoxymethyl
MPPA	monoperoxyphthalic acid
PNPBA	*p*-nitroperoxybenzoic acid
PPA	polyphosphoric acid
TFA	trifluoroacetic acid
TFAA	trifluoroacetic anhydride
TfO	trifluoromethanesulfonate
thexyl	*i*-PrCMe$_2$
TMS	trimethylsilyl
Ts	*p*-toluenesulfonyl

Table IA. Cyclization of Allyl Vinyl and Divinyl Ketones A. Acyclic Precursors

---

View PDF

Table IB. Cyclization of Allyl Vinyl and Divinyl Ketones B. Cyclic Precursors

---

View PDF

Table IC. Cyclization of Allyl Vinyl and Divinyl Ketones C. Anomalous Cyclizations

---

View PDF

Table ID. Cyclization of Allyl Vinyl and Divinyl Ketones D. Photochemical Cyclizations

---

View PDF

Table IIA. Silicon (Tin)-Directed Nazarov Cyclizations A. Acyclic Precursors

---

View PDF

Table IIB. Silicon (Tin)-Directed Nazarov Cyclizations B. Cyclic Precursors

---

View PDF

Table IIIA. Cyclizations of In Situ Generated Divinyl Ketones A. Nonacetylenes; α -Elimination

---

View PDF

Table IIIB. Cyclizations of In Situ Generated Divinyl Ketones B. Nonacetylenes; β -Elimination

---

View PDF

Table IIIC. Cyclizations of In Situ Generated Divinyl Ketones C. Acyclic Acetylenes

---

View PDF

Table IIID. Cyclizations of In Situ Generated Divinyl Ketones D. Cyclic Acetylenes

---

View PDF

Table IIIE. Cyclizations of In Situ Generated Divinyl Ketones E. α -Vinylcyclobutanones

---

View PDF

Table IVA. Cyclization of Divinyl Ketone Equivalents from Solvolysis A. Geminal Dichlorides

---

View PDF

Table IVB. Cyclization of Divinyl Ketone Equivalents from Solvolysis B. 2-Furylcarbinols

---

View PDF

Table IVC. Cyclization of Divinyl Ketone Equivalents from Solvolysis C. Vinylallenes

---

View PDF

Table VA. In Situ Construction of Divinyl Ketones A. Olefinic Acids and Anhydrides

---

View PDF

Table VB. In Situ Construction of Divinyl Ketones B. Olefinic Esters

---

View PDF

Table VC. In Situ Construction of Divinyl Ketones C. Olefinic Acid Halides and Olefins

---

View PDF

Table VD. In Situ Construction of Divinyl Ketones D. Acid Halides and Paraffins

---

View PDF

Table VE. In Situ Construction of Divinyl Ketones E. Acid Halides and Acetylenes

---

View PDF

Table VF. In Situ Construction of Divinyl Ketones F. Organometallics

---

View PDF

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS

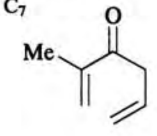
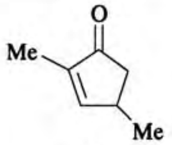
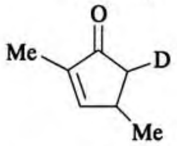
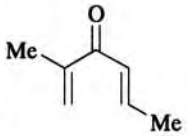
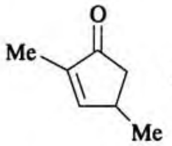
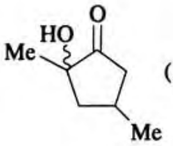
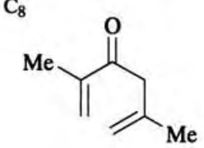
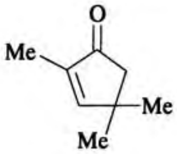
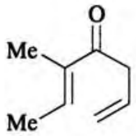
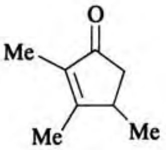
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	HCO_2H, H_3PO_4, 80°, 7 h	 (75)	5, 20
	D_3PO_4, 20°, 4-7 h	 (30)	32, 35
	H_3PO_4, 20°, 10 h	 (21) +  (11)	38
C_8 	Anhyd. HCO_2H, H_3PO_4, 40-50°, 2 h, 70-75°, 5 h	 (25)	9
	H_3PO_4 or HCl, 20°	 (—)	6

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

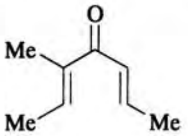
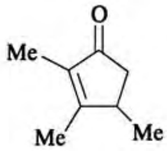
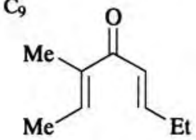
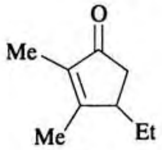
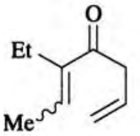
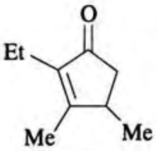
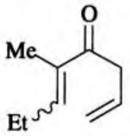
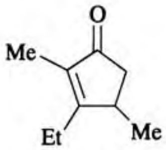
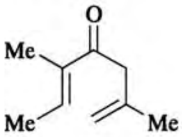
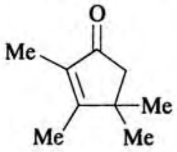
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2SO_4, 60°, 6 h	 (61)	53
C_9 	H_2SO_4, 60°, 6 h	 (37)	53
	Conc. HCl, 60°, 3 h	 (75)	12
	H_3PO_4, 60°, 2 h	 (60)	12
	H_3PO_4, 60°, 4 h	 (60)	18

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

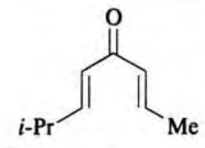
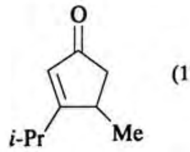
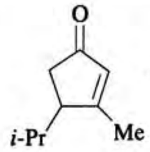
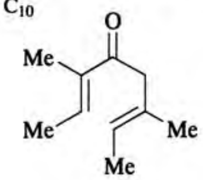
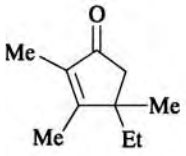
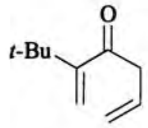
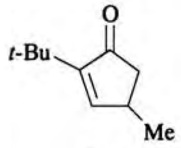
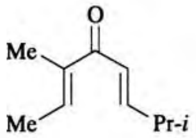
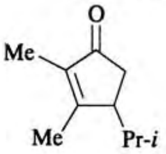
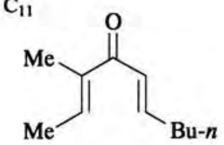
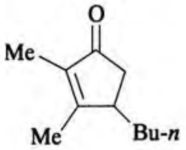
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	96% H_2SO_4, 25°	 (17) +  (11)	52
C_{10}			
	H_3PO_4 or conc. HCl, 20°, 30 min, 60°, 4 h	 (100)	10
	$HgSO_4$, H_2SO_4, MeOH 65°, 10 h	 (50)	15
	H_2SO_4 , 60°, 6 h	 (58)	53
C_{11}			
	H_2SO_4, 60°, 6 h	 (63)	53

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

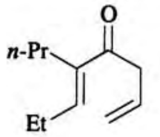
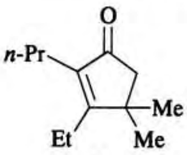
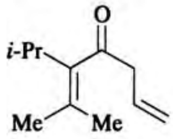
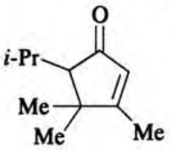
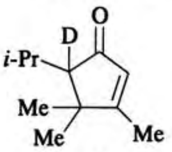
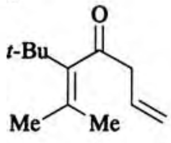
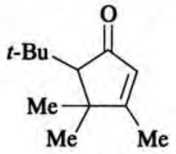
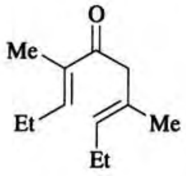
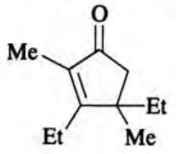
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, 60-65°, 2.5 h	 (80)	28
	H_3PO_4, 60-65°, 6 h	 (81)	27, 38
	D_2O, P_2O_5, 20°, 8 h	 (83)	36
C_{12}			
	H_3PO_4, 65°, 45 min	 (68)	25
	HCO_2H, H_3PO_4, 90°, 5 h	 (64)	19

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

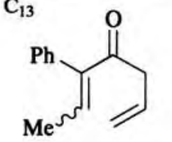
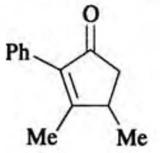
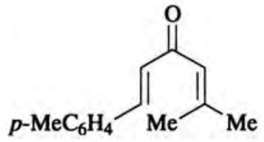
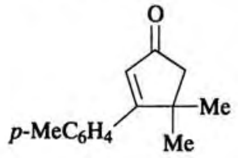
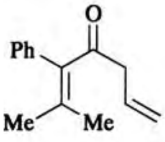
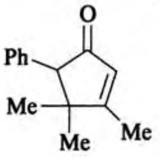
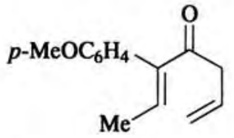
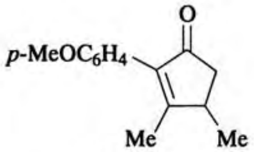
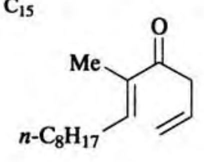
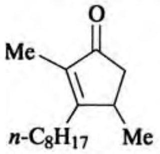
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{13} 	H_3PO_4, 60°, 1.5 h		(95)	17
	BF_3•Et_2O, C_6H_6, reflux, 72 h		(10)	68
	H_3PO_4, 70°, 40 min		(83)	24
	TsOH, 155°, 10 min		(—)	23
C_{15} 	H_3PO_4, 60°, 3 h		(94)	29

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

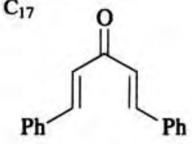
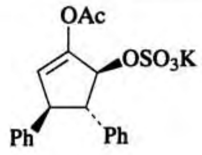
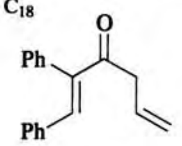
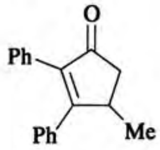
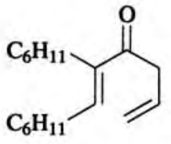
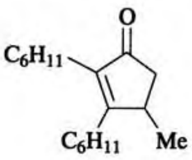
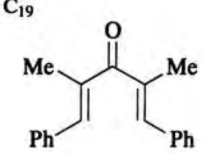
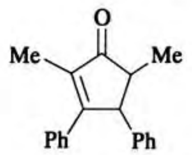
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17} 	1. H_2SO_4, Ac_2O 2. K_2CO_3		(88)	58
C_{18} 	H_3PO_4, 70-80°, 15 min		(95)	30
	H_3PO_4, 70-75°, 5 h		(50)	26
C_{19} 	Conc. HCl, EtOH, reflux, 2 h		(78)	25

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: A. ACYCLIC PRECURSORS (*Continued*)

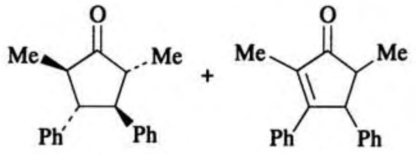
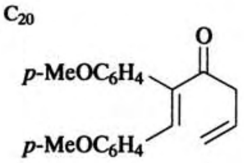
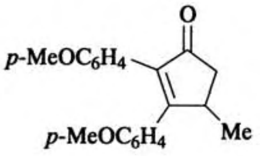
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Conc. HI, red P, reflux, 24 h	 (60) (4)	44
C_{20} 	TsOH, 180°, 20 min	 (59)	23

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS

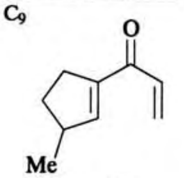
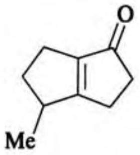
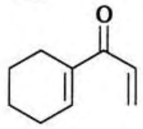
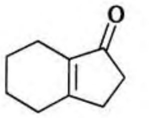
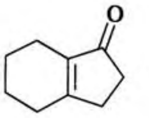
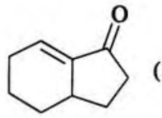
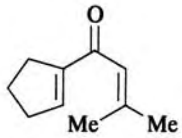
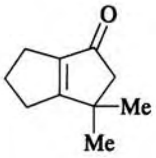
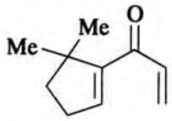
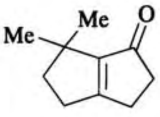
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9			
	Polyphosphoric Acid (PPA), 55-60°, 10 min	 (32)	173
	H_3PO_4, HCO_2H, 80-90°, 4 h	 (50)	39
	$FeCl_3$, CH_2Cl_2, 0°, 1.25 h	 (61) +  (17)	85
C_{10}			
	1. $SnCl_4$, CH_2Cl_2, reflux, 24 h 2. $RhCl_3$, EtOH, reflux, 2 h	 (40)	171, 179, 172
	P_2O_5, $MeSO_3H$, rt, 2 min	 (65)	179, 180

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

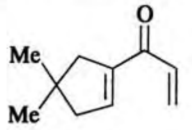
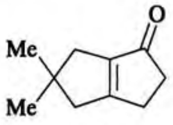
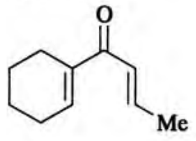
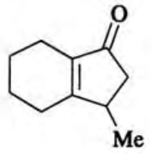
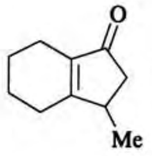
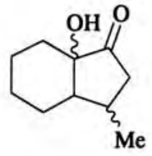
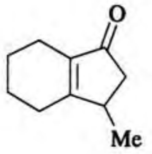
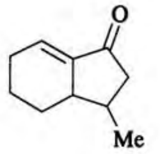
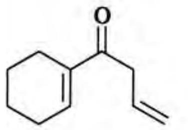
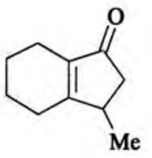
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	P_2O_5, $MeSO_3H$, 0-20°, 5 min	 (40)	148
	H_3PO_4, HCO_2H, 90°, 7 h	 (67)	39
	H_3PO_4, 15-20°, 4.5 h	 (—) +  (—)	38
	H_3PO_4, 60-65°, 6 h	 (41) +  (17)	38
	H_3PO_4, HCO_2H, 90°, 7 h	 (70)	7

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

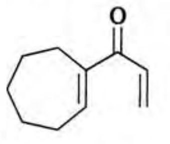
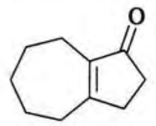
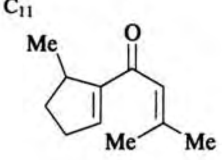
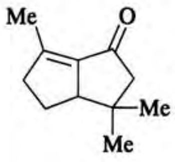
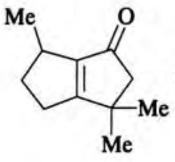
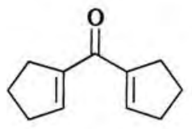
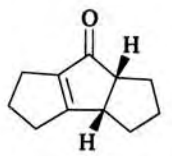
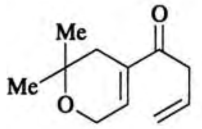
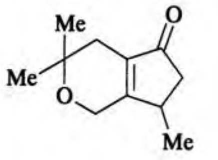
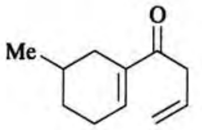
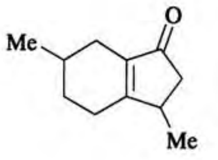
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, HCO_2H, 90°, 3 h	 (60)	77
C_{11}			
	$SnCl_4$, CH_2Cl_2, reflux, 3 d	 (33) +  (19)	68, 67
	PPA, 100°, 30 min	 (62)	71
	H_3PO_4, 65°, 4 h	 (24)	21
	H_3PO_4, 65°, 5.5 h	 (73)	104

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

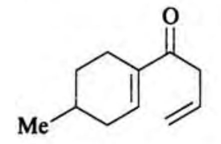
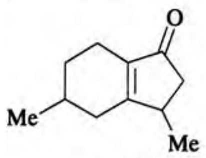
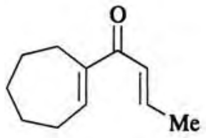
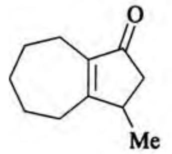
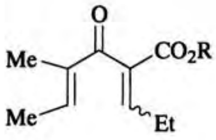
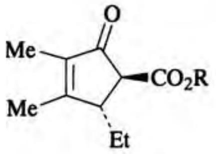
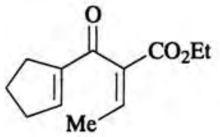
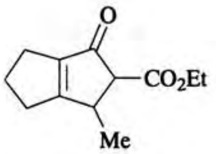
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, 60-65°, 6 h	 (73)	13
	H_3PO_4, HCO_2H, 90°, 6 h	 (75)	77
			
R			
C_{12} Et	3 equiv $SnCl_4$, CH_2Cl_2, rt, 24 h	(30)	69
Et	3 equiv TMSOTf, CH_2Cl_2, rt, 2 h	(31)	69a
C_{20} (−)-menthyl	3 equiv TMSOTf, CH_2Cl_2, rt, 2 h	(39)	69a
	3 equiv $SnCl_4$, CH_2Cl_2, rt, 24 h	 (30)	69

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

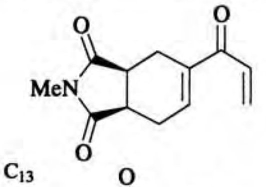
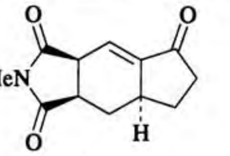
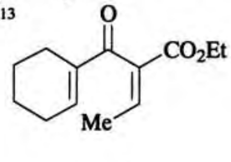
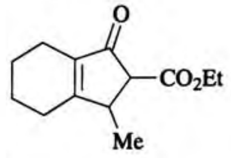
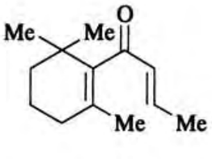
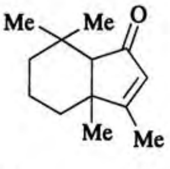
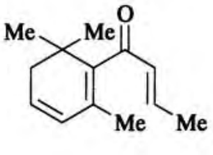
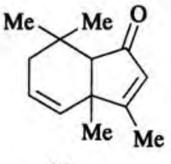
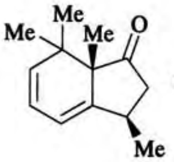
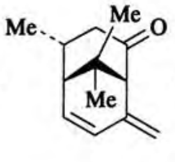
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$GaCl_3$, CH_2Cl_2, rt, 6 h	 (17)	70
C_{13} 	3 equiv TMSI, CCl_4, rt, 24 h	 (48)	69
	H_3PO_4, rt	 (80)	181
	H_3PO_4, rt	 (80)	181
	1% TsOH, 180°	 (40) +  (60)	181

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

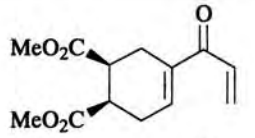
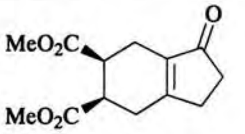
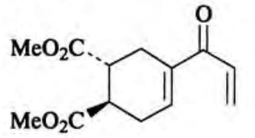
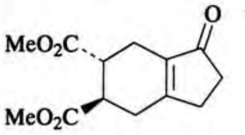
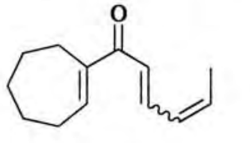
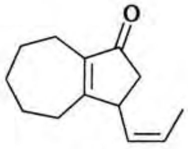
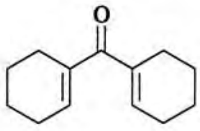
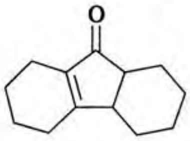
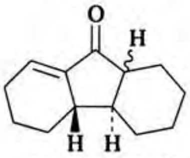
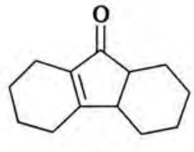
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$GaCl_3$, CH_2Cl_2, -20 to 0°, 30 min	 (73)	70
	$GaCl_3$, CH_2Cl_2, rt, 3 h	 (90)	70
	H_3PO_4, HCO_2H, 90°	 (24)	77
	H_3PO_4, HCO_2H, 90°, 10 h	 (29)	39
	HOAc, NaOAc, H_3PO_4, 68°, 3.5 h	 +  I α:β 11:89 (48) II (38)	73

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

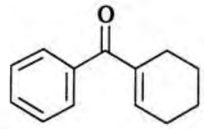
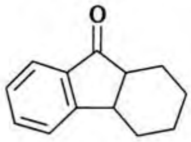
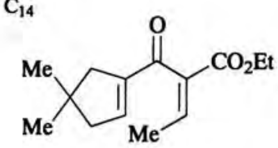
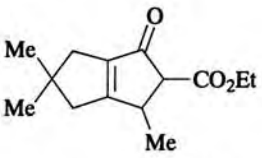
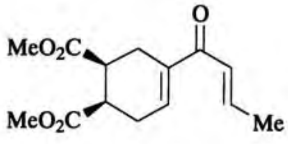
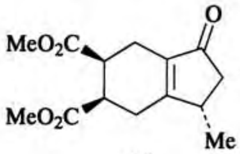
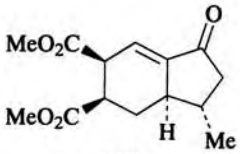
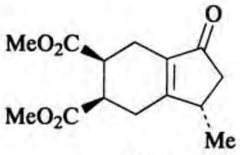
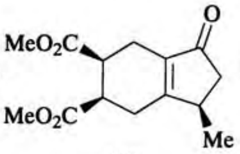
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	C_6H_6, 210°, flow system	I α:β 41:59 (33) + II (3)	73
	PPA, 100°, 15 min	 (65)	76
C_{14}			
	3 equiv $SnCl_4$, CH_2Cl_2, rt, 20 h	 (30)	41
	$GaCl_3$, CH_2Cl_2, rt, 24 h	 +  (40) (49)	70
	TsOH, C_6H_6, reflux, 6.5 h	 +  (29) (29)	70

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

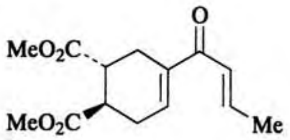
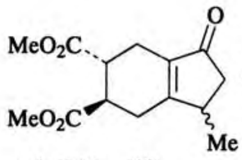
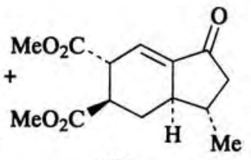
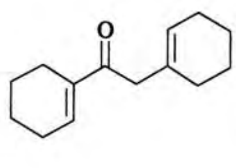
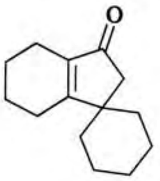
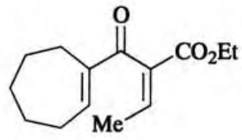
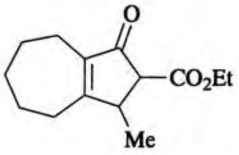
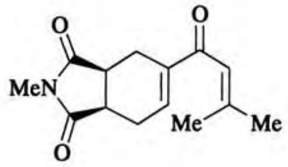
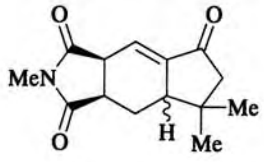
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	GaCl$_3$, CH$_2$Cl$_2$, rt, 24 h	 +  α:β 50:50 (62) (26)	70
	H$_3$PO$_4$, 60°, 6 h	 (76)	26
	2 equiv TMSI, CCl$_4$, rt, 24 h	 (35)	69
	GaCl$_3$, CH$_2$Cl$_2$, rt, 6 days	 (90) α:β 50:50	70

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

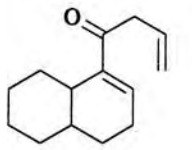
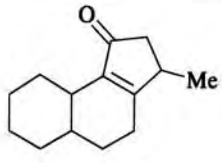
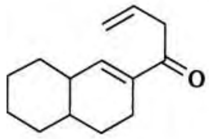
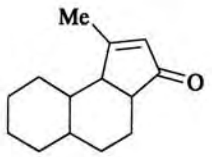
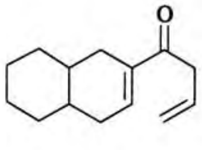
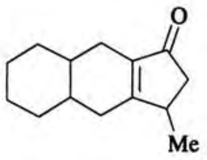
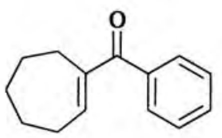
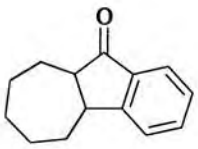
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H$_3$PO$_4$, 65°, 6.5 h	 (30)	22
	H$_3$PO$_4$, HCO$_2$H, 60-65°, 6.5 h	 (73)	11
	H$_3$PO$_4$, HCO$_2$H, 60-65°, 6h	 (—)	11
	H$_3$PO$_4$, HCO$_2$H, 90°, 6 h	 (75)	77

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

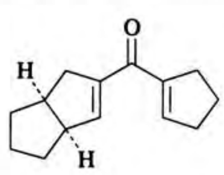
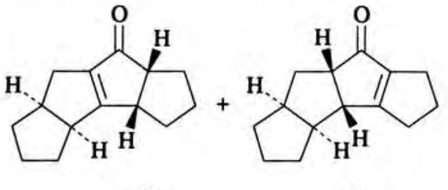
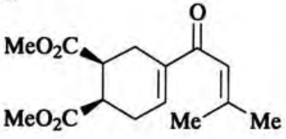
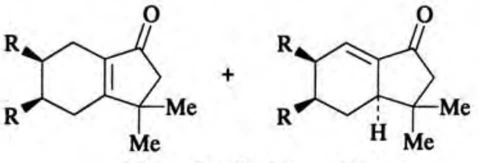
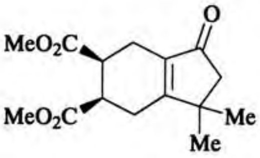
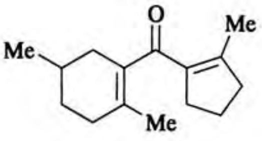
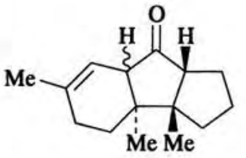
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PPA, 100°	 (48) + (12)	66
C$_{15}$ 	GaCl$_3$, CH$_2$Cl$_2$, rt, 5 days	 (68) R = CO$_2$Me (29)	70
	TsOH, toluene, reflux, 24 h	 (57)	70
	BF$_3$•OEt$_2$, CHCl$_3$, reflux 5 days	 (80) α:β 70:30	75

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

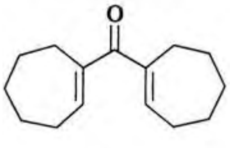
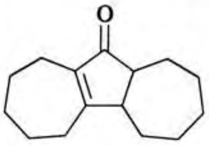
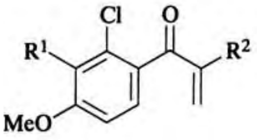
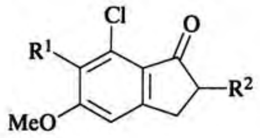
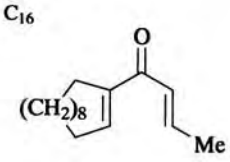
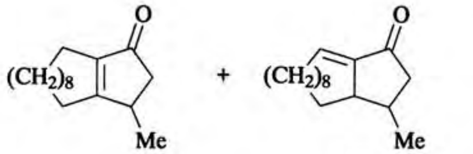
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H$_3$PO$_4$, HCO$_2$H, 0-90°, 6 h	 (50)	72
	H$_2$SO$_4$, CH$_2$Cl$_2$, 5°, 3.5 h		78
R^1 R^2			
C$_{16}$ Cl Ph		(75)	
Cl *p*-FC$_6$H$_4$		(100)	
Cl *p*-ClC$_6$H$_4$		(89)	
Cl *p*-BrC$_6$H$_4$		(94)	
C$_{17}$ Me Ph		(100)	
C$_{16}$ 	BF$_3$•OEt$_2$, C$_6$H$_6$, heat	 (48) + (18)	67

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

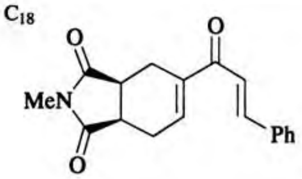
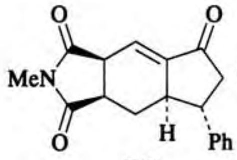
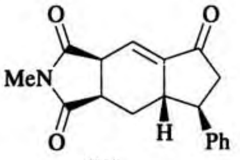
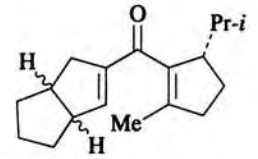
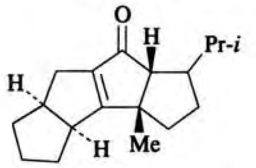
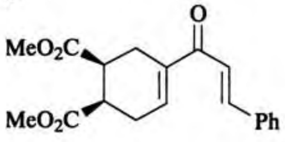
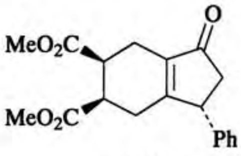
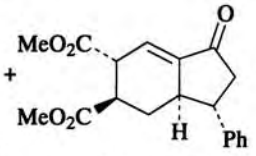
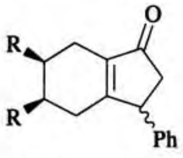
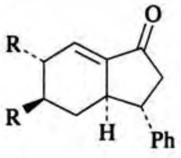
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$GaCl_3$, CH_2Cl_2, rt, 2 days	 (15) +  (31)	70
	TsOH, toluene, 110°	 (20)	66
C_{19} 	$GaCl_3$, CH_2Cl_2, rt, 5 h	 (81) +  (5)	70
	TsOH, toluene, reflux, 12 h	 +  α:β 50:50 (63) R = CO_2Me (33)	70

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: B. CYCLIC PRECURSORS (*Continued*)

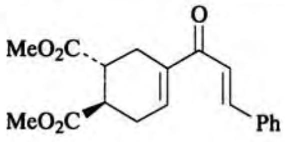
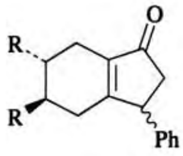
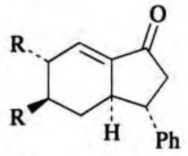
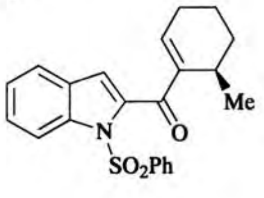
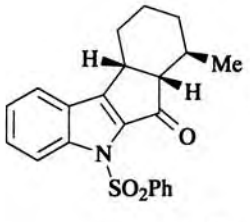
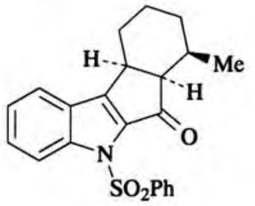
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$GaCl_3$, CH_2Cl_2, rt, 18 h	 +  (80) R = CO_2Me (4)	70
C_{22} 	$AlCl_3$, benzene, rt, 20 h	 (49) +  (24)	173a

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: C. ANOMALOUS CYCLIZATIONS

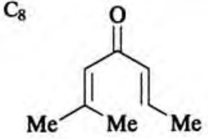
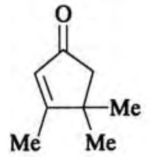
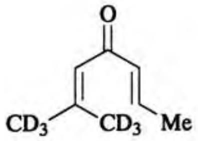
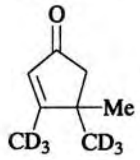
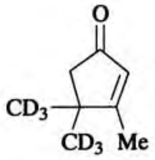
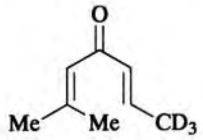
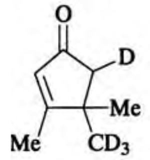
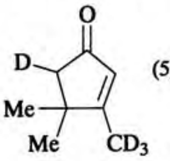
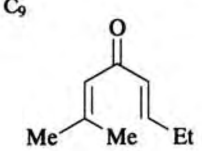
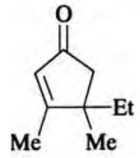
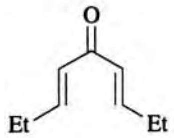
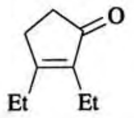
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_8$ 	H_2SO_4, 60°, 6 h	 (46)	53
	H_2SO_4, 60°, 6 h	 (14) +  (6)	53
	H_2SO_4, 60°, 6 h	 (50) +  (5)	53
C$_9$ 	H_2SO_4, 60°, 6 h	 (39)	53
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (77)	80, 79

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: C. ANOMALOUS CYCLIZATIONS *(Continued)*

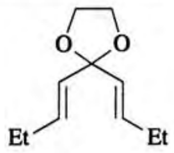
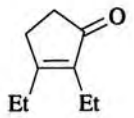
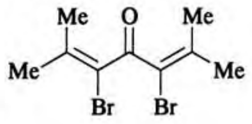
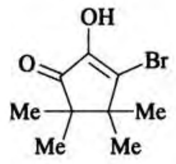
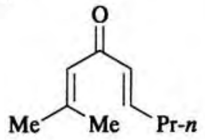
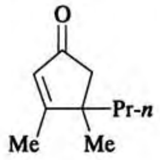
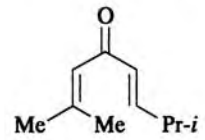
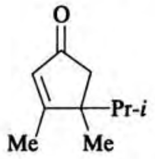
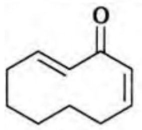
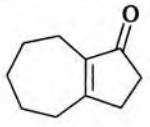
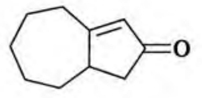
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (67)	79
	H_2SO_4, 20°, 10 min	 (75)	43
C$_{10}$ 	H_2SO_4, 60°, 6 h	 (55)	53
	H_2SO_4, 60°, 6 h	 (31)	53
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (58) +  (6)	80, 79

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: C. ANOMALOUS CYCLIZATIONS *(Continued)*

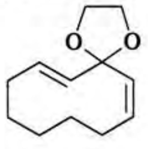
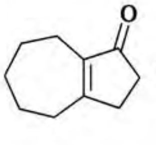
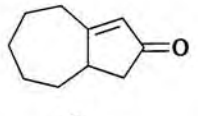
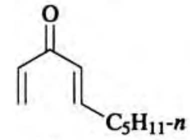
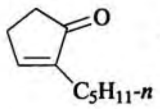
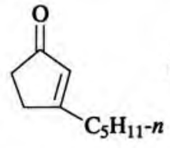
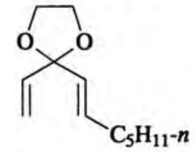
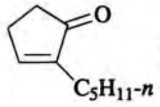
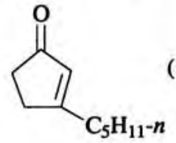
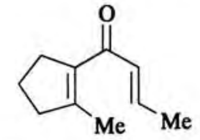
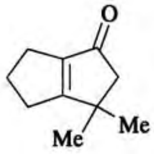
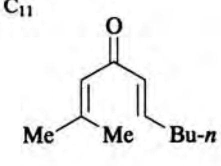
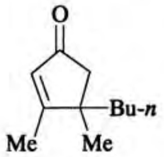
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (47) +  (37)	80, 79
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (18) +  (2)	80, 79
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (14) +  (1)	80, 79
	$AlCl_3$, CH_2Cl_2, reflux, 4 h	 (40)	157a
C_{11} 	H_2SO_4, 60°, 6 h	 (47)	53

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: C. ANOMALOUS CYCLIZATIONS *(Continued)*

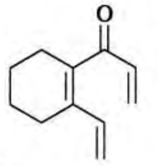
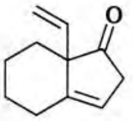
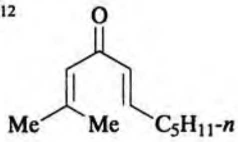
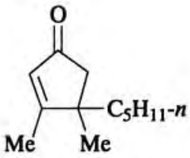
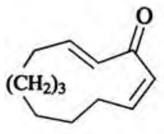
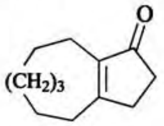
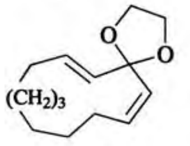
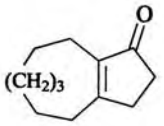
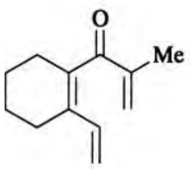
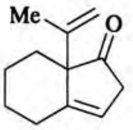
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$FeCl_3$, CH_2Cl_2, -15°, 30 min	 (19)	81
C_{12} 	H_2SO_4, 60°, 6 h	 (47)	53
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (67)	79, 80
	H_3PO_4, HCO_2H, 90°, 2-3 h	 (63)	80, 79
	$FeCl_3$, CH_2Cl_2, -15°, 30 min	 (16)	81

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: C. ANOMALOUS CYCLIZATIONS *(Continued)*

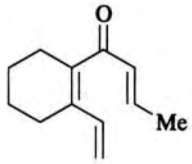
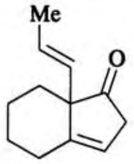
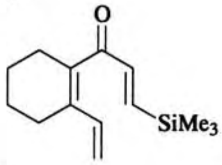
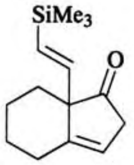
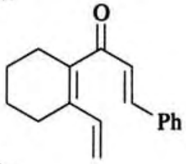
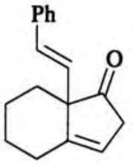
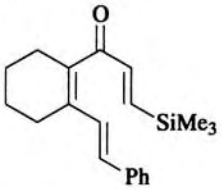
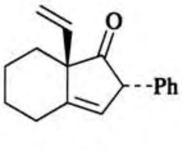
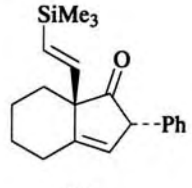
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$FeCl_3$, CH_2Cl_2, 0°, 30 min	 (61)	81
C_{14} 	$FeCl_3$, CH_2Cl_2, -10°, 30 min	 (59)	81
C_{17} 	$FeCl_3$, CH_2Cl_2, 0°, 30 min	 (65)	81
C_{20} 	$FeCl_3$, CH_2Cl_2, 0°, 5 min	 (44) +  (34)	81

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: D. PHOTOCHEMICAL CYCLIZATIONS

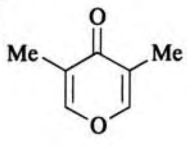
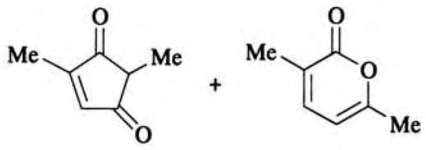
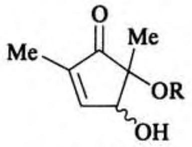
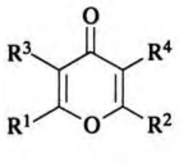
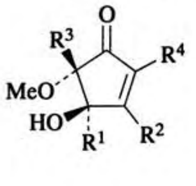
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	hν	 minor major (—)	182
	hν, ROH	 R = Me (—) R = CH_2CF_3 (—)	182
	hν, MeOH		83
R^1 R^2 R^3 R^4			
H Me OMe H		(—)	
Me H OMe H		(—)	
C_8 Me Me Me H		(—)	
C_9 Me Me Me Me		(—)	

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: D. PHOTOCHEMICAL CYCLIZATIONS *(Continued)*

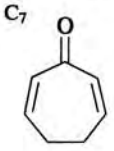
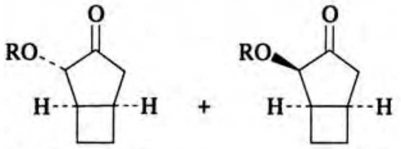
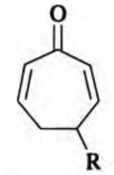
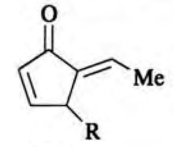
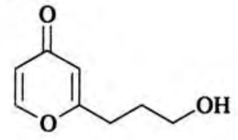
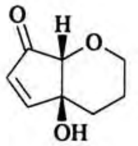
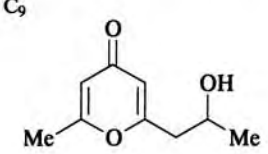
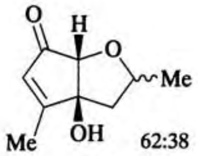
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 			60
	$h\nu$, HOAc, 20 h	R = OAc (30) (30)	
	$h\nu$, t-BuOH, H_2SO_4	R = OBu-t (30) (30)	
	1. $h\nu$, FSO_3H, CCl_4 2. $NaHCO_3$		183
		R = H (—)	
		R = Me (—)	
C_8 	$h\nu$, CF_3CH_2OH	 (43)	83a
C_9 	$h\nu$, CF_3CH_2OH	 62:38 (75)	83a

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: D. PHOTOCHEMICAL CYCLIZATIONS *(Continued)*

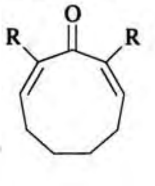
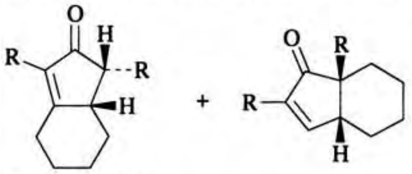
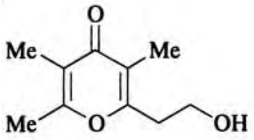
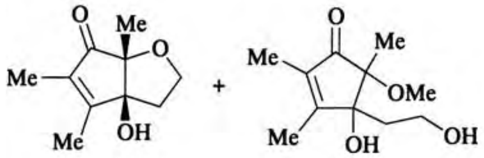
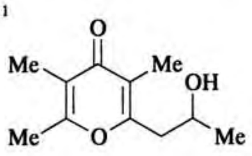
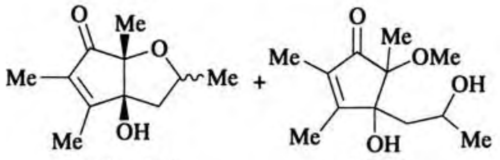
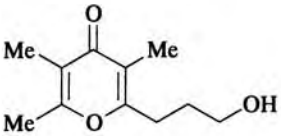
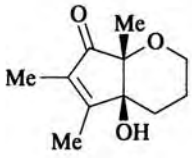
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$h\nu$, H_2SO_4		61
		R = H (71) (29)	
		R = D (71) (29)	
C_{10} 			
	$h\nu$, CH_3OH	(60) (14-16)	83a
	$h\nu$, CF_3CH_2OH	(75) (0)	83a
C_{11} 			
	$h\nu$, CH_3OH	(64) 66:34 (14-16)	83a
	$h\nu$, CF_3CH_2OH	(84) 66:34 (0)	83a
	$h\nu$, CF_3CH_2OH	 (99)	83a

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: D. PHOTOCHEMICAL CYCLIZATIONS *(Continued)*

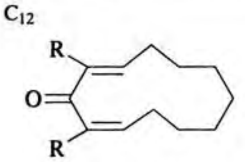
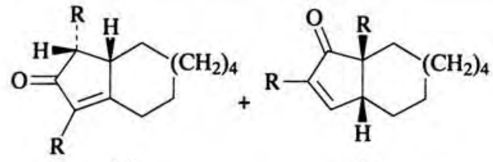
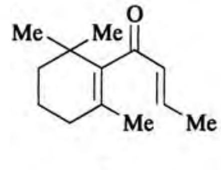
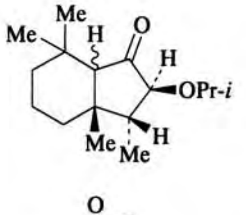
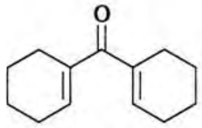
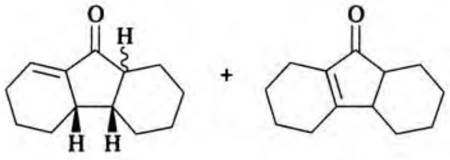
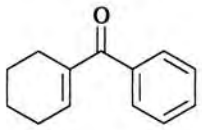
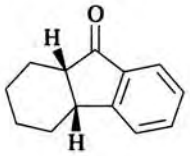
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{12}			
 R = H R = D	$h\nu$, H_2SO_4	 (70) (30) (70) (30)	61
C_{13}			
	$h\nu$, i-PrOH	 (—)	62
	$h\nu$, C_6H_6	 (56) (7)	73
	$h\nu$, C_6H_6	 (65)	82a

TABLE I. CYCLIZATION OF ALLYL VINYL AND DIVINYL KETONES: D. PHOTOCHEMICAL CYCLIZATIONS *(Continued)*

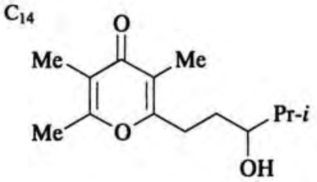
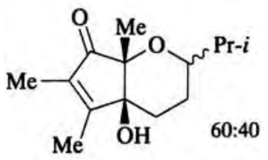
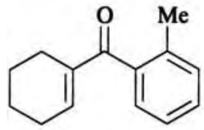
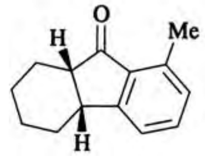
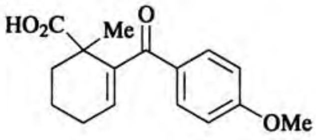
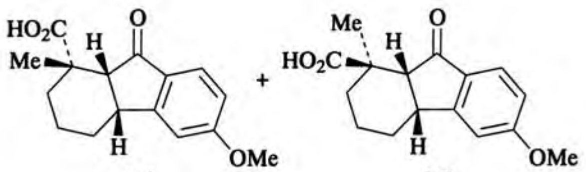
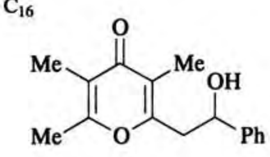
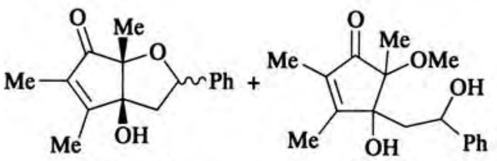
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14}			
	$h\nu$, CF_3CH_2OH	 60:40 (61)	83a
	$h\nu$, C_6H_6	 (57)	82a
C_{15}			
	$h\nu$, C_6H_6	 (50) (50)	82b
C_{16}			
			
	$h\nu$, CH_3OH	(76) 50:50 (14-16)	83a
	$h\nu$, CF_3CH_2OH	(92) 50:50 (0)	83a

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: A. ACYCLIC PRECURSORS

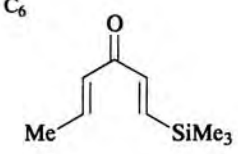
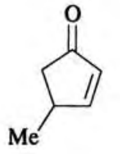
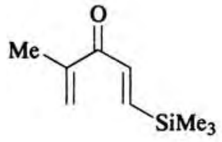
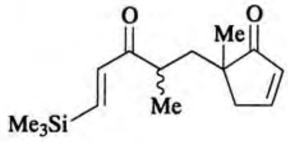
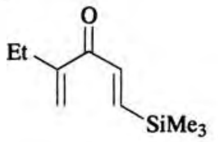
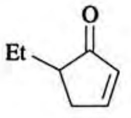
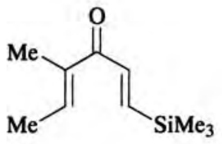
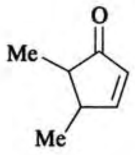
Reactant	Conditions	Product(s) and Yield(s) (%)			Refs.
C_6					
	FeCl$_3$, CH$_2$Cl$_2$, 20°, 12 h			(54)	85
	FeCl$_3$, CH$_2$Cl$_2$, -20°, 6 h			(42)	85
C_7					
	FeCl$_3$, CH$_2$Cl$_2$, 0°				85
	Concentration of divinyl ketone (M)				
	0.08 2 h			(—)	
	0.02 8 h			(33)	
	0.004 48 h			(51)	
	FeCl$_3$, CH$_2$Cl$_2$, -10°, 0.5 h		*cis:trans* 59:41	(95)	85

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: A. ACYCLIC PRECURSORS (*Continued*)

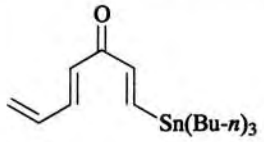
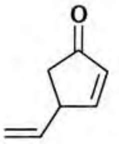
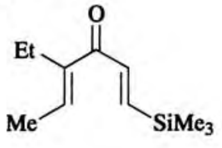
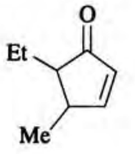
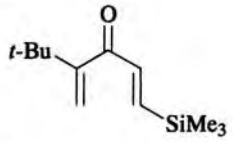
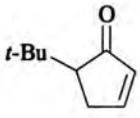
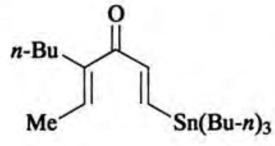
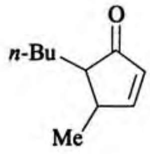
Reactant	Conditions	Product(s) and Yield(s) (%)			Refs.
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 20°			(21)	99
C_8					
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 1 h		*cis:trans* 41:59	(70)	85
C_9					
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 1 h			(97)	85
C_{10}					
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 20°		*cis:trans* 37:63	(93)	99

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: A. ACYCLIC PRECURSORS (*Continued*)

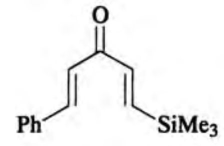
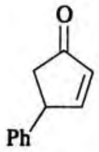
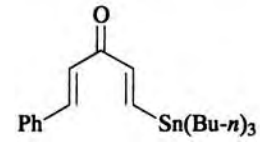
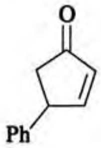
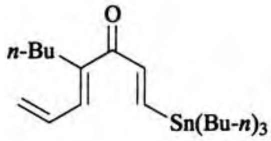
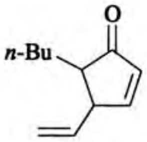
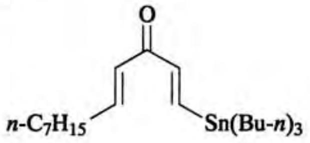
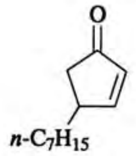
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{11}			
	$FeCl_3$, toluene, 20°, 12 h	 (27)	85
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 (44)	99
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 *cis:trans* 43:57 (97)	99
C_{12}			
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 (47)	99

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: A. ACYCLIC PRECURSORS (*Continued*)

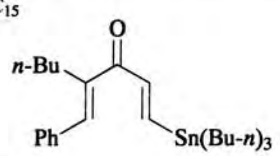
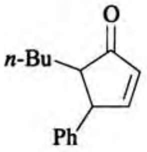
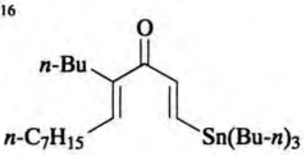
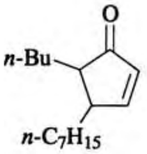
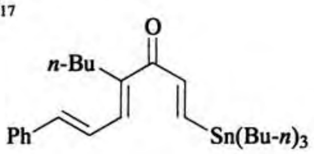
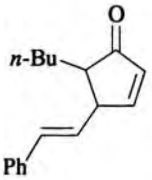
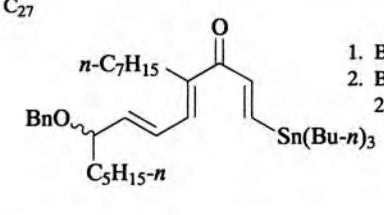
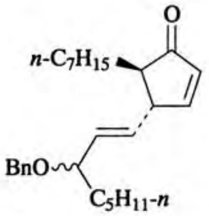
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{15}			
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 *cis:trans* 42:58 (92)	99
C_{16}			
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 *cis:trans* 42:58 (87)	99
C_{17}			
	$BF_3{\bullet}OEt_2$, CH_2Cl_2, 20°	 *cis:trans* 40:60 (83)	99
C_{27}			
	1. $BF_3{\bullet}OEt_2$, CH_2Cl_2, 20° 2. Basic Al_2O_3, CH_2Cl_2, rt 24 h	 (56)	99

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS

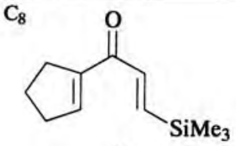
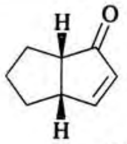
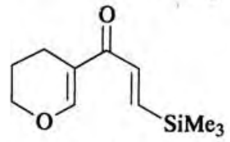
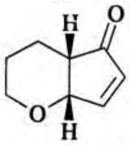
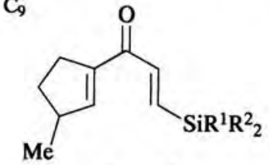
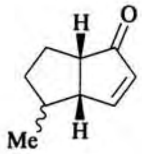
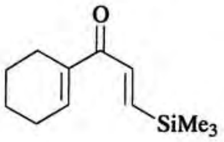
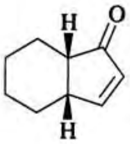
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8 	$FeCl_3$, $(CH_2Cl)_2$, 20°, 2.5 h		(52)	85
	$FeCl_3$, CH_2Cl_2, 20°, 8 h		(60)	88
C_9 	$FeCl_3$, CH_2Cl_2, 20°			87
R^1 R^2		β:α		
Me Me	2.5 h	54:46	(50)	
Ph Me	3 h	59:41	(46)	
Me Ph	2 h	62:38	(41)	
Ph Ph	4 h	76:24	(13)	
i-Pr *i*-Pr	4 h	79:21	(13)	
	$FeCl_3$, CH_2Cl_2, 0°, 4 h		(84)	85

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

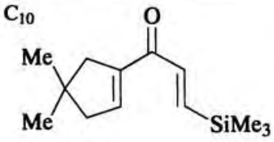
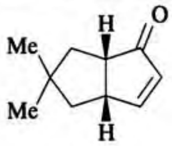
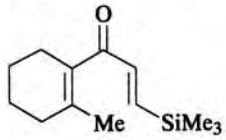
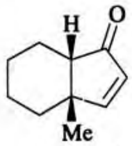
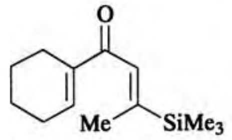
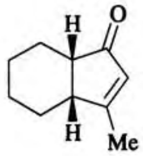
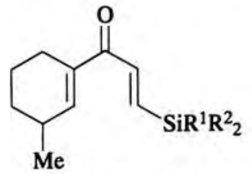
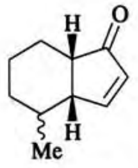
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{10} 	$FeCl_3$, CH_2Cl_2, 20°, 2.5 h		(83)	184
	$FeCl_3$, CH_2Cl_2, 20°, 13 h		(70)	88
	$FeCl_3$, CH_2Cl_2, 20°, 12 h		(76)	88
	$FeCl_3$, CH_2Cl_2			87
R^1 R^2		β:α		
Me Me	0°, 4 h	78:22	(99)	
Ph Me	20°, 2 h	84:16	(63)	
Me Ph	20°, 2 h	86:14	(83)	
Ph Ph	20°, 2 h	87:13	(15)	
i-Pr *i*-Pr	20°, 4 h	90:10	(70)	

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

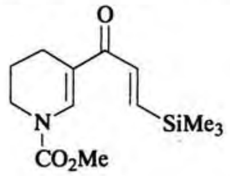
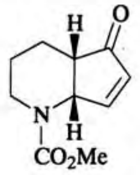
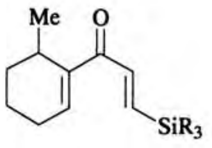
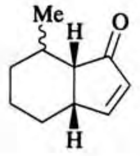
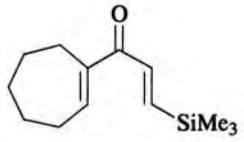
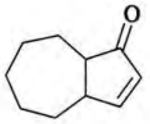
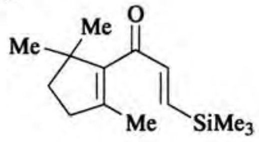
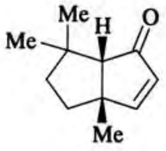
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	ZrCl$_4$, (CH$_2$Cl)$_2$, 60°, 36 h		(76)	88
	FeCl$_3$, CH$_2$Cl$_2$			86
R		β:α		
Me	0°, 4 h	72:28	(85)	
i-Pr	20°, 2 h	78:22	(78)	
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 1 h		*cis:trans* 85:15 (74)	85
C$_{11}$				
	BF$_3$•OEt$_2$, toluene, 100°, 36 h		(70)	95

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

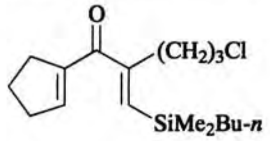
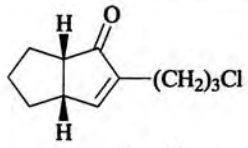
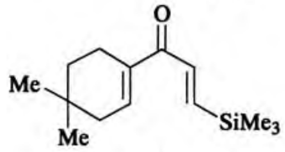
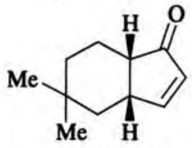
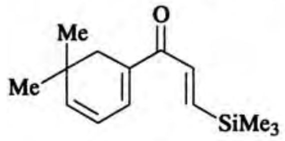
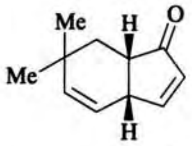
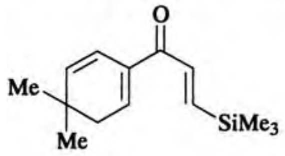
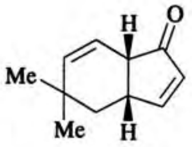
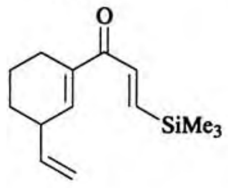
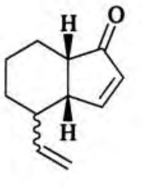
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	SnCl$_4$, -78°, 1 h		(100)	97
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 4 h		(78)	88
	FeCl$_3$, CH$_2$Cl$_2$, 20°, 2 h		(69)	88
	FeCl$_3$, CH$_2$Cl$_2$, -15°, 1 h		(69)	88
	FeCl$_3$, CH$_2$Cl$_2$, -10°, 2 h		β:α 78:22 (66)	87

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

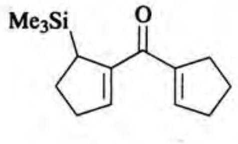
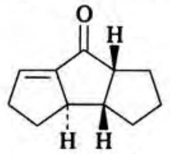
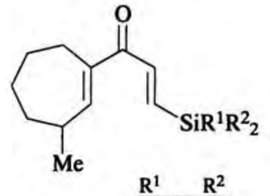
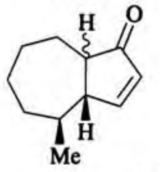
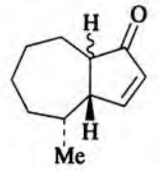
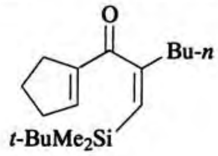
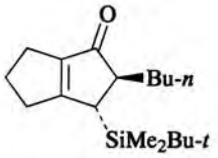
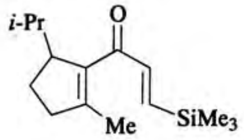
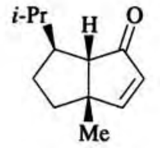
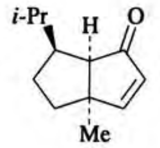
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 10°, 10 min		(77)	89
	FeCl$_3$, CH$_2$Cl$_2$, 0°	 +		98
R^1 R^2		β:α	β:α	
Me Me	1 h	(47) 71:29	(36) 100:0	
Ph Me	1 h	(44) 71:29	(33) 98:2	
Me Ph	1 h	(29) 73:27	(29) 98:2	
C$_{12}$ Ph Ph	2 h	(27) 70:30	(17) 100:0	
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$,-78°; -20°, 4 h; 0°, 24 h		(69)	97
	BF$_3$•OEt$_2$, C$_6$H$_6$, 90°, 20 h	 (60) +	 (12)	185

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

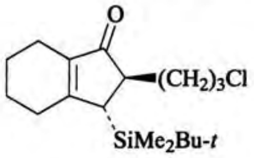
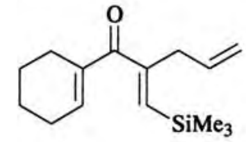
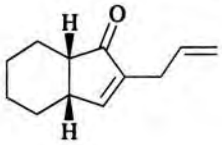
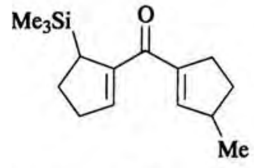
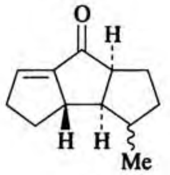
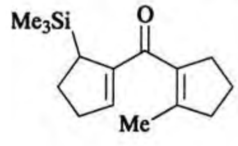
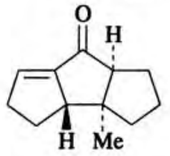
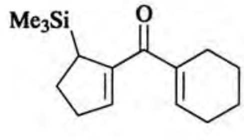
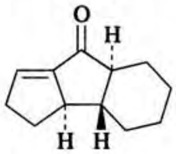
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$,-78°; -20°, 4 h; 0°, 24 h		(80)	97
	FeCl$_3$, CH$_2$Cl$_2$, -25°, 1 h		(76)	88
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 10°, 1 h	 53:47	(83)	89
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 20°, 3 h		(79)	89
	FeCl$_3$, CH$_2$Cl$_2$, -20°, 45 min		(36)	89

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

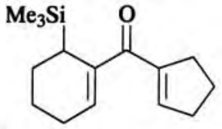
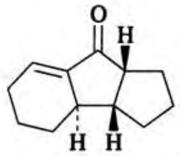
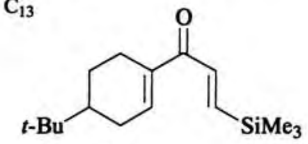
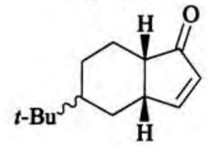
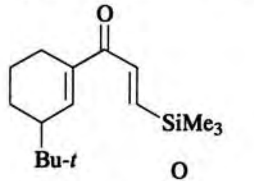
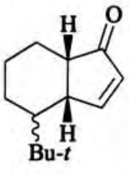
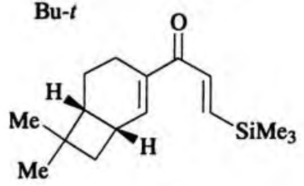
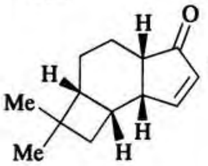
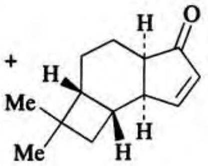
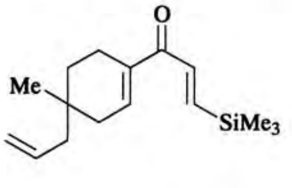
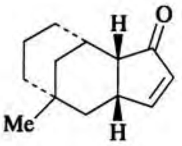
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	FeCl$_3$, CH$_2$Cl$_2$, -50°, 15 min		(88)	89
C$_{13}$				
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 4 h	 β:α 76:24	(82)	86
	FeCl$_3$, CH$_2$Cl$_2$, 0°, 8 h	 β:α 94:6	(63)	87
	FeCl$_3$, CH$_2$Cl$_2$, -25°, 2 h	 (60) +  (9)		88
	FeCl$_3$, CH$_2$Cl$_2$, 0-20°, 1 h		(44)	88

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

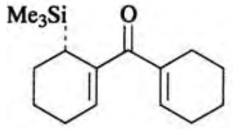
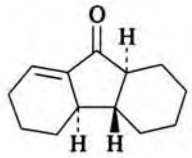
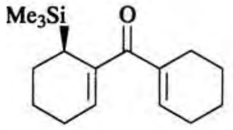
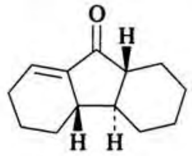
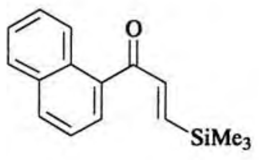
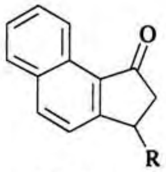
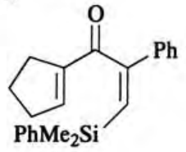
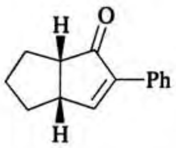
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
 (*S*)-(–)	FeCl$_3$, CH$_2$Cl$_2$, -50°, 1 min		(72)	90, 89
 (*R*)-(+)	FeCl$_3$, CH$_2$Cl$_2$, -50°, 1 min		(58)	90, 89
				85
	FeCl$_3$, (CH$_2$Cl)$_2$, 20°, 12 h	R = SiMe$_3$	(70)	
	FeCl$_3$, toluene, 20°, 48 h	R = H	(60)	
C$_{14}$				
	FeCl$_3$, CH$_2$Cl$_2$, -25°, 3 h		(86)	88

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

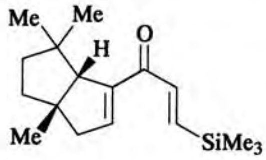
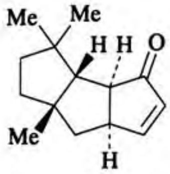
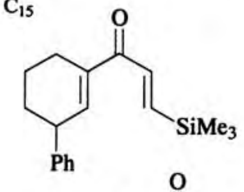
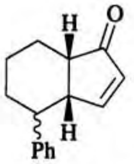
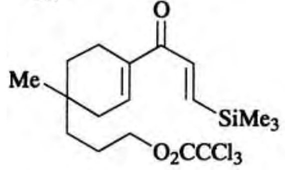
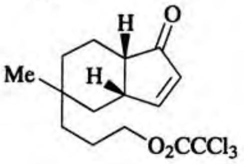
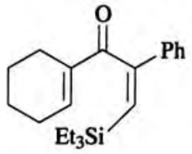
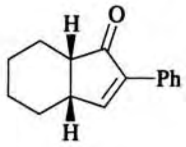
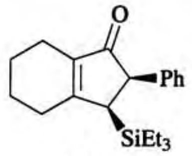
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	BF_3•OEt_2, toluene, 20°, 6 h		(80)	95
C_{15} 	$FeCl_3$, CH_2Cl_2, 0°, 4 h		β:α 94:6 (76)	87
	$FeCl_3$, CH_2Cl_2, 0°, 4 h		(78)	88
		 +		97
	BF_3•OEt_2, CH_2Cl_2, -78°; -20°, 4 h; 0°, 24 h	(30)	(37)	
	$SnCl_4$, CH_2Cl_2, -78°, 2 h	(18)	(18)	
	$FeCl_3$, CH_2Cl_2, 0°, 4 h	(18)	(24)	

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

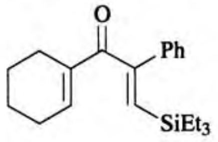
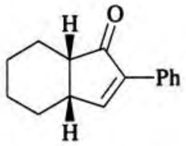
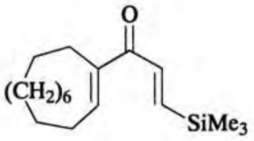
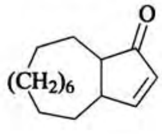
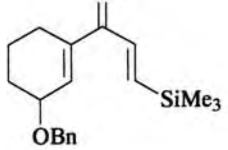
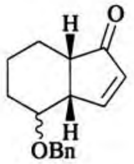
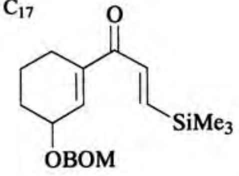
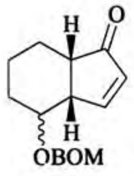
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	$FeCl_3$, CH_2Cl_2, -25°, 3 h		(86)	98
	$FeCl_3$, CH_2Cl_2, 0°, 2 h		*cis:trans* 46:54 (78)	85
C_{16} 	$FeCl_3$, CH_2Cl_2, 0°, 2 h		β:α 94:6 (76)	87
C_{17} 	$FeCl_3$, CH_2Cl_2, 0°, 2 h		β:α 93:7 (40)	87

TABLE II. SILICON(TIN)-DIRECTED NAZAROV CYCLIZATIONS: B. CYCLIC PRECURSORS (*Continued*)

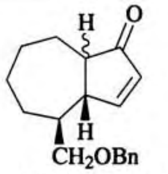
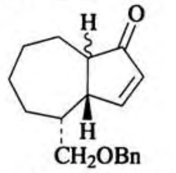
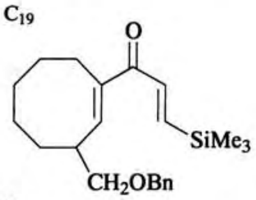
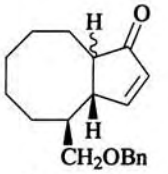
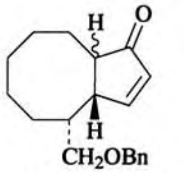
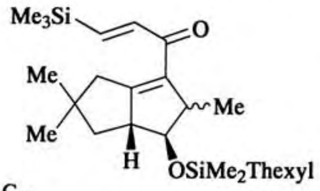
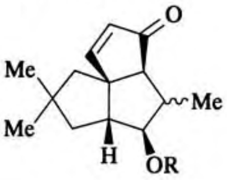
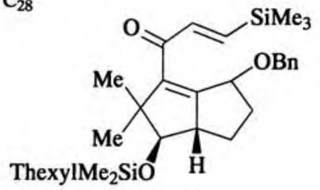
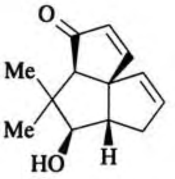
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{18} 	$FeCl_3$, CH_2Cl_2, 0°, 1 h	 β:α 62:38 (8) +  β:α 85:15 (72)	98
C_{19} 	$FeCl_3$, CH_2Cl_2, 0°, 1 h	 β:α 57:43 (15) +  β:α 97:3 (73)	98
C_{22} 	BF_3•OEt_2, C_6H_5Et, reflux	 R = $SiMe_2$Thexyl (38) R = H (22)	100a
C_{28} 	BF_3•OEt_2, C_6H_5Et, reflux	 (53)	100

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: A. NON-ACETYLENES; α-ELIMINATION

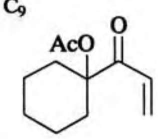
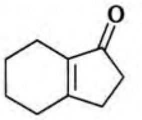
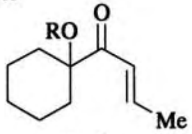
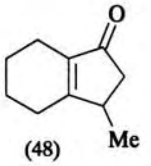
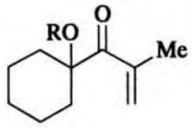
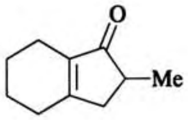
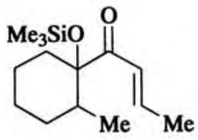
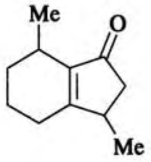
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_9 	TsOH, toluene, 112°	 (41)	101
C_{10}  R = H R = Me$_3$Si R = Ac	TsOH, toluene, 112°	 (48) (48) (53)	101
 R = Me$_3$Si R = Ac	TsOH, toluene, 112°	 (19) (65)	101
C_{11} 	TsOH, toluene, 112°	 (22)	186

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: A. α-ELIMINATION *(Continued)*

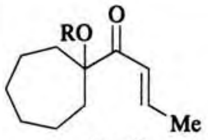
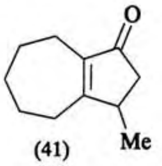
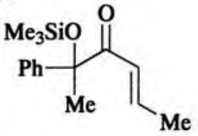
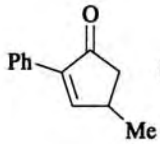
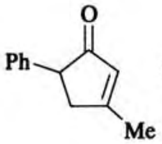
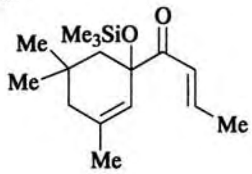
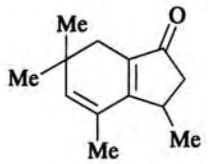
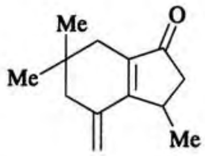
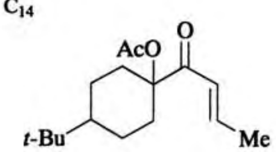
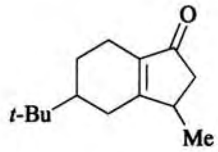
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 R = H R = Ac	TsOH, toluene, 112°	 (41) (60)	101
C_{12} 	TsOH, toluene, 112°	 (37) +  (41)	101
C_{13} 	TsOH, toluene, 112°	 +  (56) (24)	101
C_{14} 	TsOH, toluene, 112°	 (66)	101

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: A. α-ELIMINATION *(Continued)*

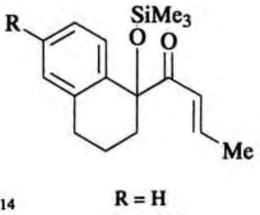
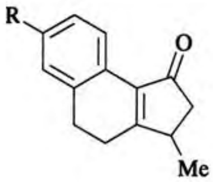
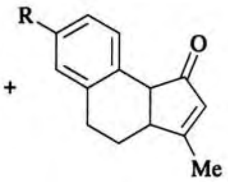
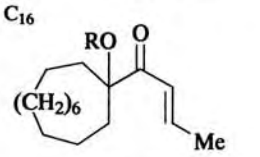
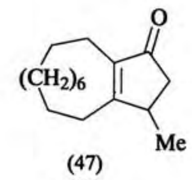
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 C_{14} R = H C_{15} R = OMe	TsOH, toluene, 112°	 +  (50) (50) (23) (77)	101
C_{16}  R = H R = OAc	TsOH, toluene, 112°	 (47) (91)	101

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: B. NON-ACETYLENES; β-ELIMINATION

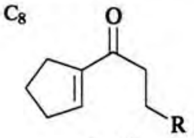
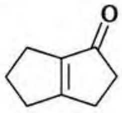
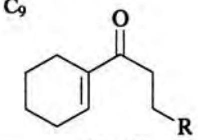
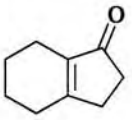
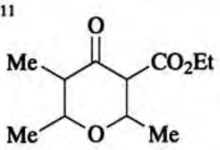
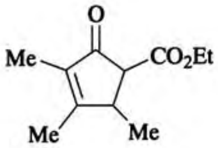
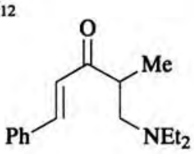
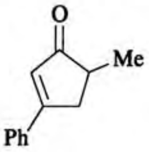
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8 			
R = Cl	H_3PO_4, HCO_2H, 90°, 12 h	(97)	103
R = NEt_2	H_3PO_4, HCO_2H, 80-90°, 6 h	(15)	104
C_9 			
R = Cl	H_3PO_4, HCO_2H, 90°, 3 h	(72)	102
R = NEt_2	H_3PO_4, HCO_2H, 80-90°, 6 h	(45)	104
C_{11} 			
	Me_3SiCl, NaI, DMF, 120°, 6 h	(59)	105
	Me_3SiOTf, CH_2Cl_2, rt, 2 h	(55)	69a
C_{12} 	H_3PO_4, HCO_2H, 80-90°, 6 h	 (50)	104

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: B. β-ELIMINATION *(Continued)*

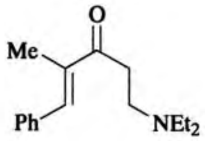
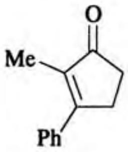
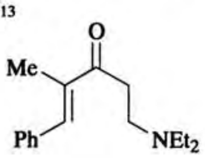
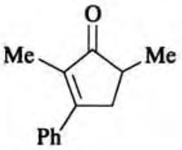
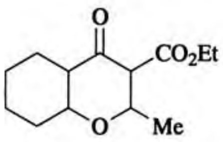
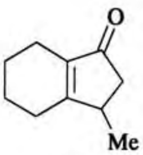
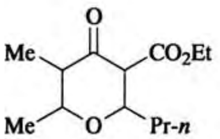
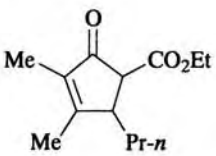
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_3PO_4, HCO_2H, 80-90°, 6 h	 (45)	104
C_{13} 	H_3PO_4, HCO_2H, 80-90°, 6 h	 (30)	104
			
	Me_3SiCl, NaI, DMF, 120°, 5 h	(77)	105
	Me_3SiOTf, CH_2Cl_2, rt, 2 h	(77)	69a
	Me_3SiCl, NaI, DMF, 120°, 7 h	 (68)	105

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: B. β-ELIMINATION *(Continued)*

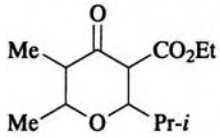
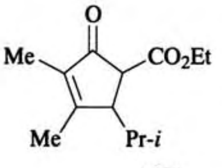
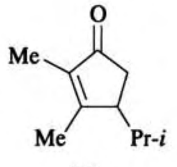
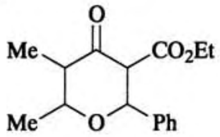
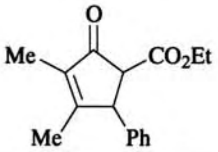
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Me_3SiCl, NaI, DMF, 120°, 10 h	 (32) +  (44)	105
C_{16}			
	Me_3SiCl, NaI, DMF, 120°, 10 h	 (64)	105

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: C. ACYCLIC ACETYLENES

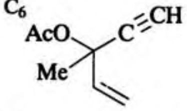
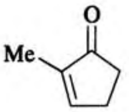
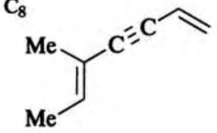
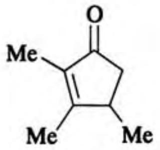
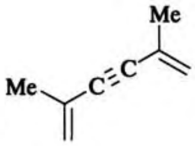
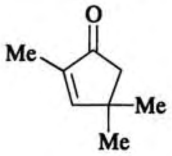
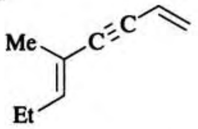
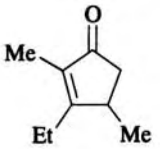
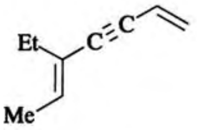
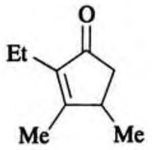
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6 	$PdCl_2(MeCN)_2$, HOAc, MeCN, 60-80°		(50-61)	142
C_8 	conc. HCl, 60-70°, 4 h		(71)	4, 6
	H_3PO_4, 40-50°, 2 h; 60-65°, 5 h		(52)	9
C_9 	conc. HCl, 60-70°, 4 h		(70)	4
	conc. HCl, 60-70°, 4 h		(70)	4

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: C. ACYCLIC ACETYLENES (*Continued*)

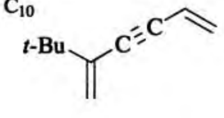
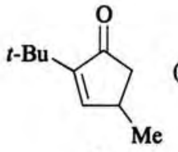
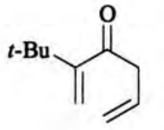
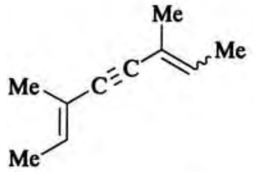
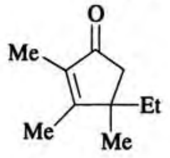
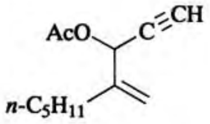
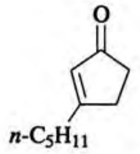
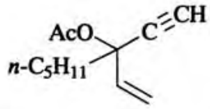
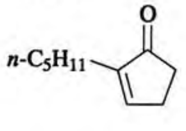
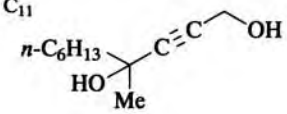
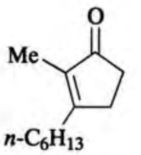
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	90% MeOH, H_2SO_4, $HgSO_4$, 60-70°, 4 h	 (49) +  (14)	15
	H_3PO_4, 70°, 5 h	 (100)	10
	$PdCl_2(MeCN)_2$, HOAc, MeCN, 60-80°	 (65-73)	31
	$PdCl_2(MeCN)_2$, HOAc, MeCN, 60-80°	 (48-66)	31
C_{11} 	MeOH, H_2SO_4, 0°, 1.7 h	 (58)	147

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: C. ACYCLIC ACETYLENES (*Continued*)

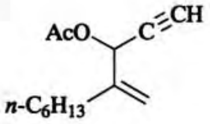
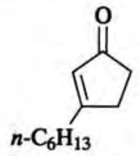
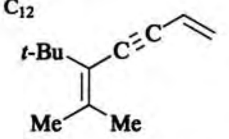
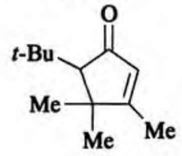
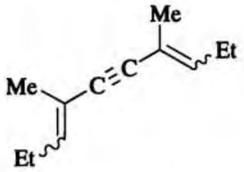
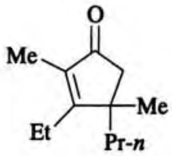
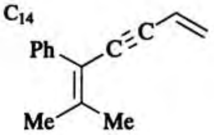
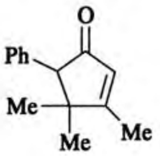
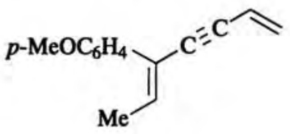
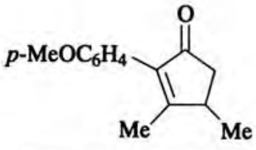
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	$PdCl_2(MeCN)_2$, HOAc, MeCN, 60-80°	 (63)	142
C_{12} 	H_3PO_4, 60-65°, 30 min	 (9)	25
	HCO_2H, H_3PO_4, 90°	 (65-70)	19
C_{14} 	H_3PO_4, 70-80°, 3 h	 (9)	24
	1. $HgSO_4$, H_2SO_4, MeOH, 65°, 12 h 2. *p*-TsOH, 155°, 10 min	 (57)	23

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES

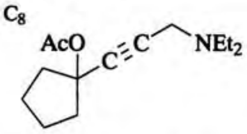
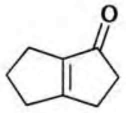
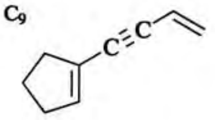
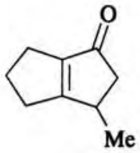
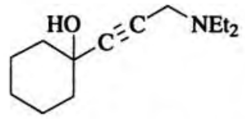
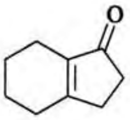
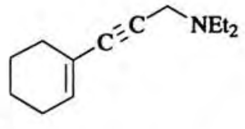
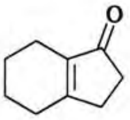
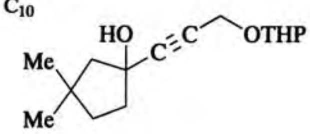
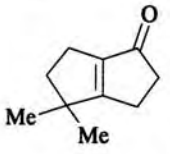
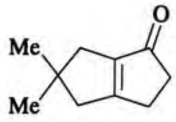
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_8 	H_3PO_4, HCO_2H, reflux, 5 h		(7)	155
C_9 	H_3PO_4, 55-60°		(31)	8
	H_3PO_4, HCO_2H, reflux; $Hg(OAc)_2$, reflux, 4 h		(52)	155
	H_3PO_4, HCO_2H, reflux; $Hg(OAc)_2$, reflux, 4 h		(48)	155
C_{10} 	P_2O_5, $MeSO_3H$, 0°, 5 min	 (—) +  1:1	(—)	148

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES *(Continued)*

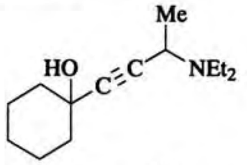
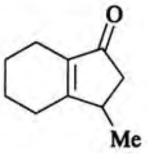
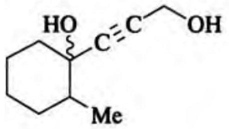
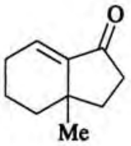
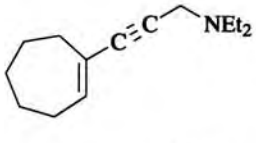
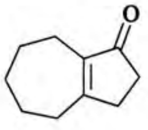
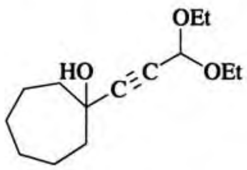
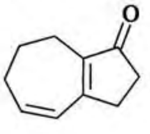
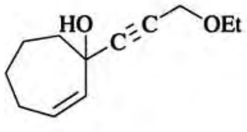
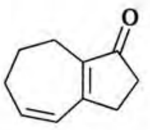
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_3PO_4, HCO_2H, reflux, 6 h		(51)	155
	H_2SO_4, MeOH, 0°, 30 min		(70)	147, 149
	H_3PO_4, HCO_2H, reflux, 6 h		(8)	155
	1. $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0°, 0.5 h 2. H_2SO_4, EtOH, 0°, 0.5-1 h		(25)	156
	1. Ac_2O, pyridine, rt, 1.5 h 2. H_2SO_4, MeOH, -15°, 2.5 h		(49)	147

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

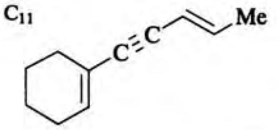
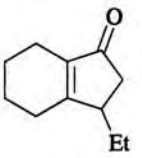
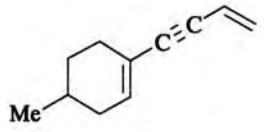
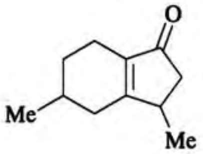
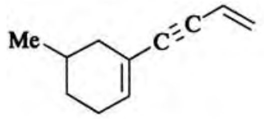
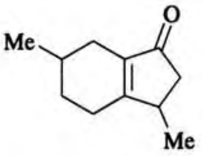
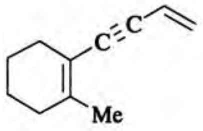
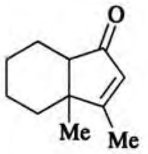
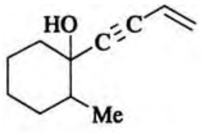
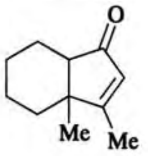
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{11} 	HgO, BF_3•OEt_2, Cl_3CCO_2H, MeOH, 20-50°		(28)	187
	H_3PO_4, 65°, 6 h		(70)	13
	H_3PO_4, 65°, 6 h		(70)	14
	H_3PO_4, 60-65°, 6 h		(65)	31
	H_3PO_4		(~60)	31

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

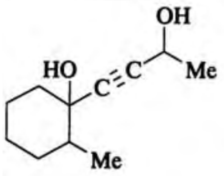
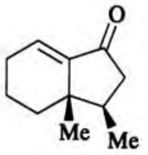
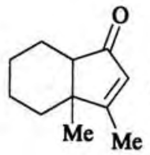
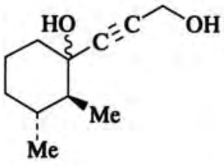
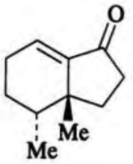
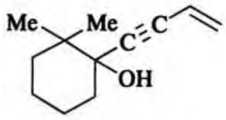
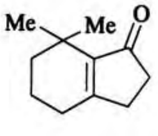
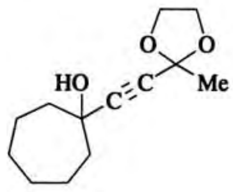
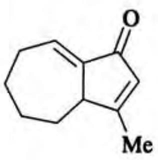
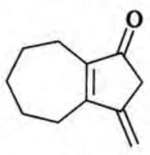
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2SO_4, MeOH, 0°, 30 min	 (67) + 	(10)	147, 149
	1. Ac_2O, pyridine, rt, 50, min 2. H_2SO_4, CF_3CH_2OH, 0-20°, 12 h		(60)	147, 149
	P_2O_5, $MeSO_3H$, -15°, 10 min		(53)	145
	1. $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0°, 0.5 h 2. H_2SO_4, EtOH, 0°, 0.5-1 h	 (27) +  (23)		156

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

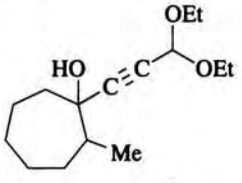
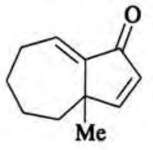
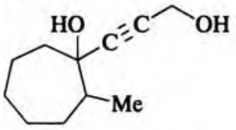
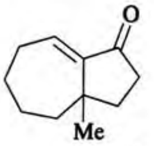
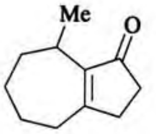
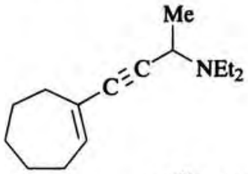
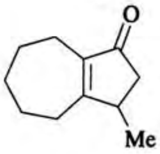
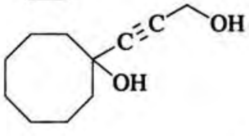
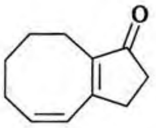
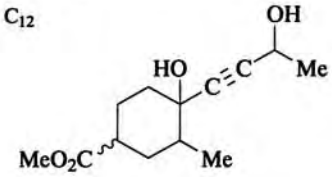
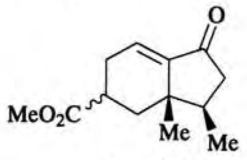
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0°, 0.5 h 2. H_2SO_4, EtOH, 0°, 0.5-1 h	 (51)	156
	H_2SO_4, MeOH, 0°, 4 h	 (67) +  (14)	147
	H_3PO_4, HCO_2H, reflux, 4 h	 (35)	155
	1. Ac_2O, pyridine, rt, 1 h 2. H_2SO_4, MeOH, -15°, 25 min	 (42)	147
C_{12} 	H_2SO_4, MeOH, 50°, 30 min	 β:α 60:40 (49-60)	188, 147

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

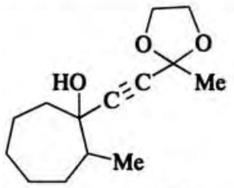
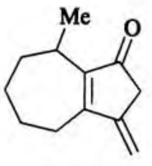
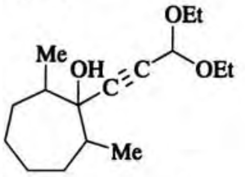
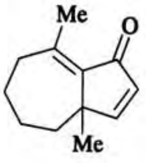
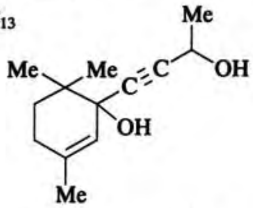
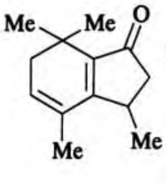
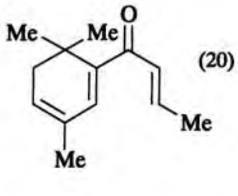
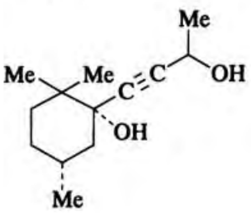
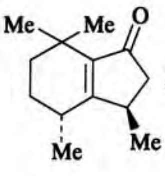
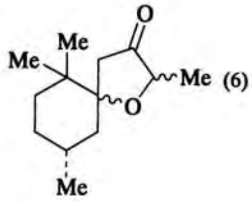
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $MeSO_2Cl$, Et_3N, CH_2Cl_2, 0°, 0.5 h 2. H_2SO_4, EtOH, 0°, 0.5-1.0 h	 (23)	156
	H_2SO_4, EtOH, 0°, 0.5-1.0 h	 (73)	156
C_{13} 	HCO_2H, H_2O, 90°, 20 min	 (10) +  (20)	151
	HCO_2H, H_2O, 90°, 20 min	 (19) +  (6)	151

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES *(Continued)*

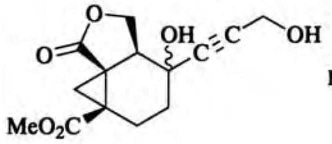
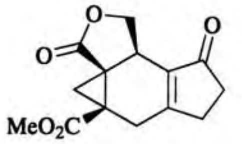
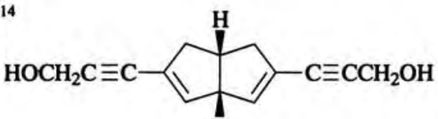
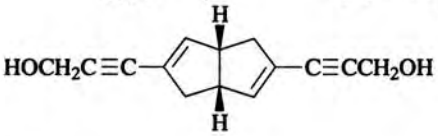
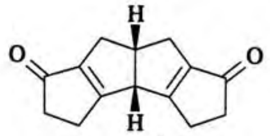
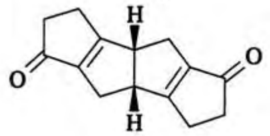
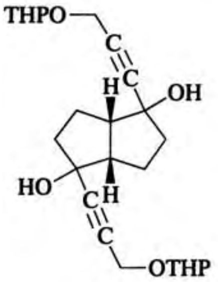
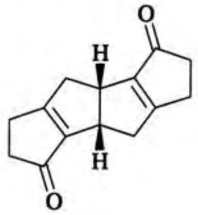
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	P_2O_5, $MeSO_3H$, rt, 2.5 h		(34)	150
C_{14}				
 47:53 + 	P_2O_5, $MeSO_3H$, rt	 + 	(31) (46)	143
	1. Amberlite, MeOH 2. P_2O_5, $MeSO_3H$, rt, 5 h		(25)	146

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES *(Continued)*

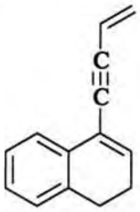
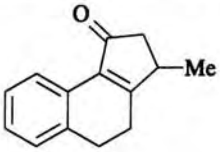
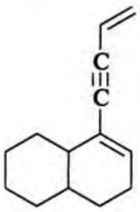
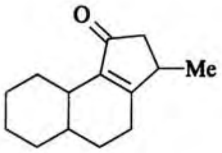
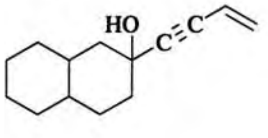
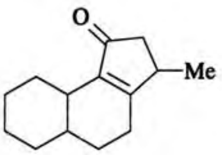
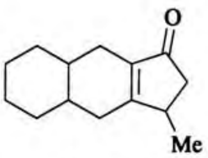
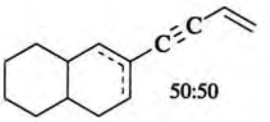
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2SO_4, $HgSO_4$, MeOH, 60°, 10 h		(48)	22
	H_3PO_4, 65°, 7 h		(27)	22
	H_3PO_4, 70°, 12 h	 +  (40) (50)		34, 11
 50:50	H_3PO_4, 65-70°, 6 h	" (—) + " (—)		11

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

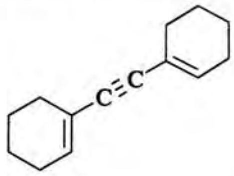
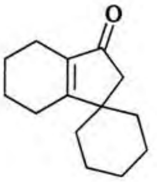
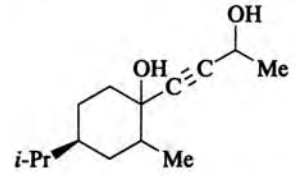
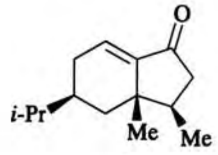
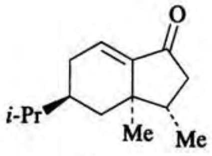
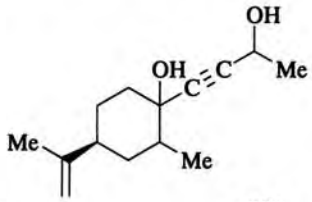
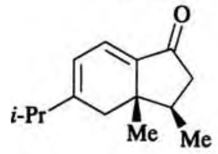
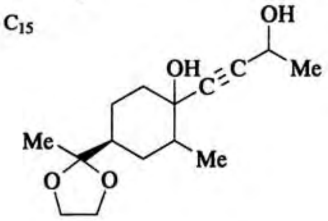
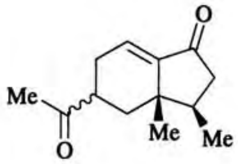
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HCO_2H, 55-60°, 10 h	 (70)	26
	H_2SO_4, MeOH, 0°, 30 min	 (54) +  (10)	147, 149
	H_2SO_4, MeOH, 0°, 30 min	 (55)	147, 188
C_{15} 	H_2SO_4, MeOH, 0°, 30 min	 (34)	147

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

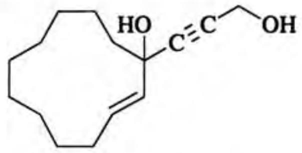
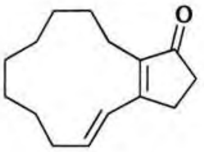
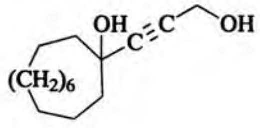
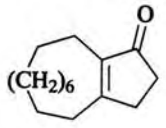
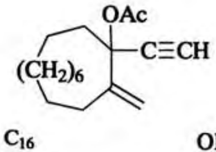
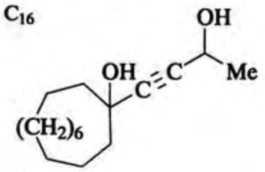
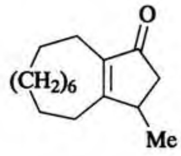
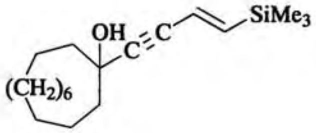
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	H_2SO_4, MeOH, 0°, 30 min	 (65)	147, 153
	Cation resin KU-2, HOAc, reflux, 15 h	 (73)	154
	$PdCl_2(MeCN)_2$, HOAc, MeCN, 60-80°	" (78-89)	142
C_{16} 	HOAc, H_2SO_4	 (—)	152
	HOAc, H_2SO_4, 50-60°, 10 min	" (64)	141

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: D. CYCLIC ACETYLENES (*Continued*)

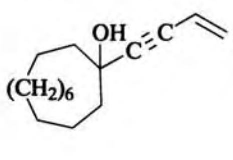
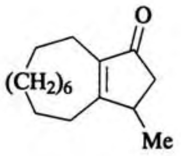
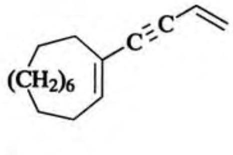
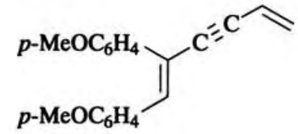
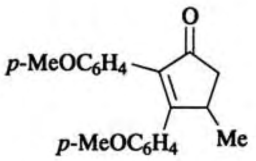
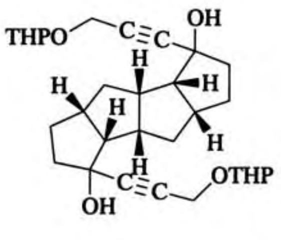
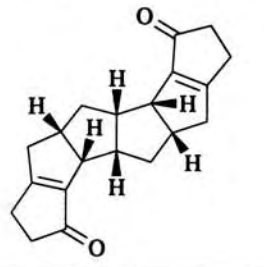
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	H_2SO_4, HOAc, (1:10), reflux, 2 h H_2SO_4, HOAc, (1:20), reflux, 2 h Cation resin KU-2, HOAc, reflux, 15 h		(73) (75) (80)	140
	P_2O_5, H_3PO_4, heptane, 90°, 8 h H_2SO_4, HOAc (1:9), 100°, 13 h	" (79) " (45)		140
C_{20}				
	H_2SO_4, $HgSO_4$, MeOH, 65°, 6 h		(60)	23
	1. Amberlite, MeOH 2. P_2O_5 , $MeSO_3H$, rt, 5 h		(45)	146

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: E. α-VINYLCYCLOBUTANONES

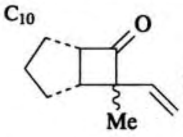
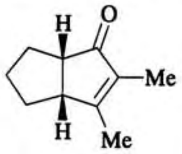
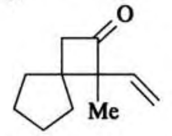
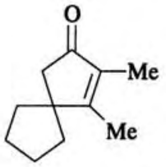
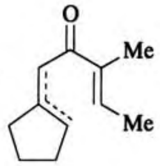
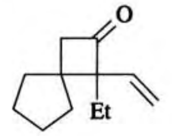
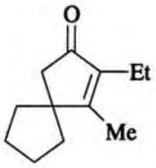
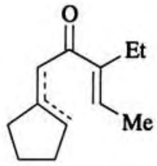
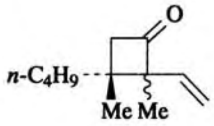
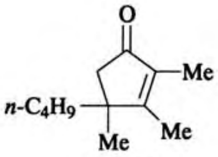
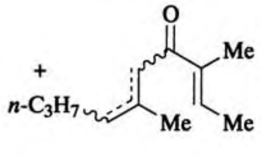
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
 Me α:β 70:30	$MeSO_3H$, rt, 30 min $MeSO_3H$, $CDCl_3$, 60°, 30 min	 (46) (76)	107, 108
C_{11}			
	$MeSO_3H$, CH_2Cl_2, rt, 26 h	 (71) +  (8)	107, 108
C_{12}			
	$MeSO_3H$, CH_2Cl_2, rt, 2 h	 (51) +  (20)	107, 108
 Me α:β 50:50	$MeSO_3H$, CH_2Cl_2, rt, 16 h	 (65) +  (11)	107, 108

TABLE III. CYCLIZATIONS OF IN SITU GENERATED DIVINYL KETONES: E. α-VINYLCYCLOBUTANONES *(Continued)*

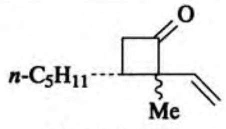
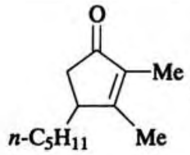
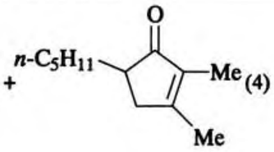
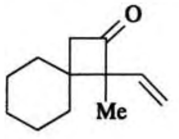
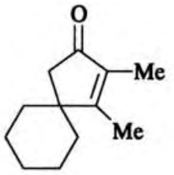
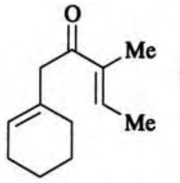
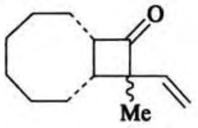
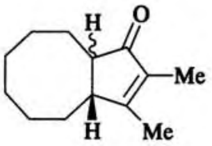
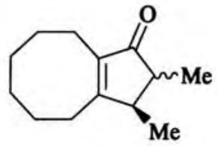
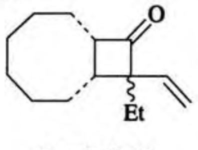
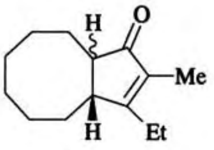
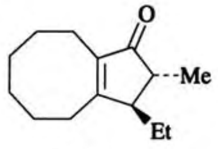
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
 Me α:β 70:30	$MeSO_3H$, CH_2Cl_2, 0°, 65 min	 (51) +  (4)	107, 108
	$MeSO_3H$, CH_2Cl_2, rt, 24 h	 (66) +  (4)	107, 108
C_{13}			
 Me α:β 75:25	$MeSO_3H$, rt, 30 min	 +  (43) 76:24 (15) 58:42	107, 108
C_{14}			
 Et α:β 85:15	$MeSO_3H$, rt, 4 h	 +  (39) 69:31 (15)	107, 108

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: A. GEMINAL DICHLORIDES

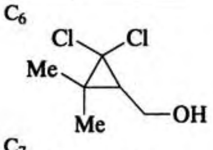
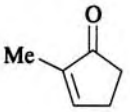
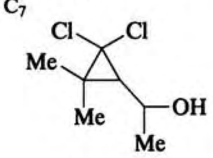
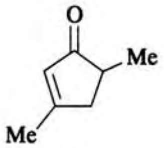
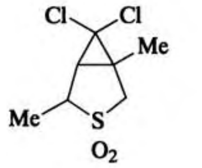
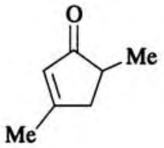
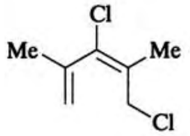
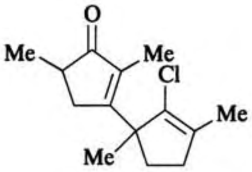
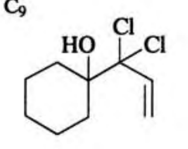
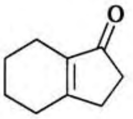
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6 	47% HBr, 100°, 2 h		(44)	141, 109
C_7 	47% HBr, 100°, 2 h		(83)	141, 109
	80% HOAc, reflux, 1-3 h		(67)	112
	80% HOAc, reflux		(55-60)	189
C_9 	TFA, rt, 1.5 h		(71)	110, 109

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: A. DICHLORIDES *(Continued)*

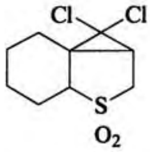
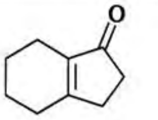
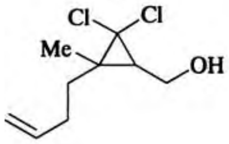
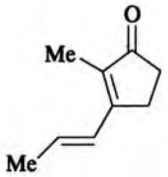
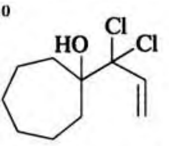
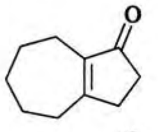
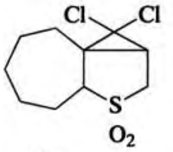
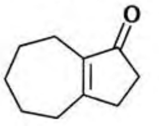
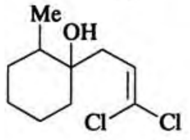
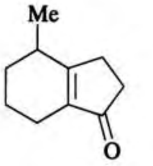
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	80% HOAc, reflux		(48)	112
	47% HBr, 100°, 2 h		(70)	111, 109
C_{10}				
	TFA, rt, 1.5 h		(87)	110, 109
	80% HOAc, reflux		(80)	112
	TFA, rt, 2.5 h		(47)	109

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: A. DICHLORIDES *(Continued)*

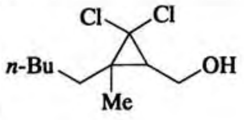
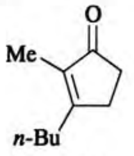
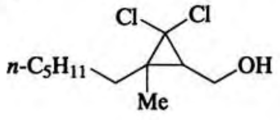
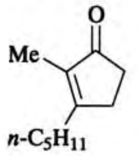
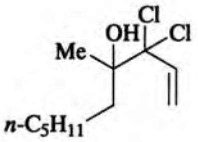
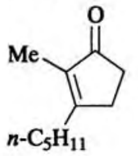
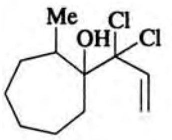
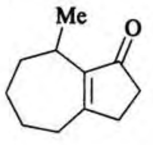
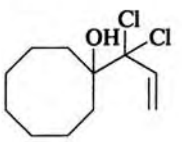
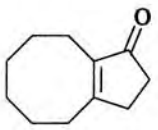
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	47% HBr, 100°, 2 h		(56)	111, 109
C_{11}				
	47% HBr, 100°, 2 h		(59)	111, 109
	TFA, rt, 1.5 h		(87)	109
	TFA, rt, 1.5 h		(58)	110, 109
	TFA, rt, 1.5 h		(80)	110, 109

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: A. DICHLORIDES *(Continued)*

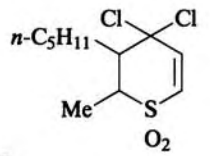
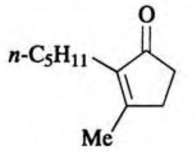
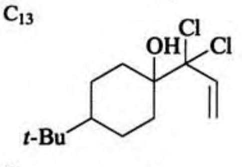
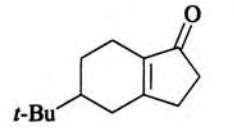
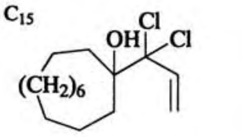
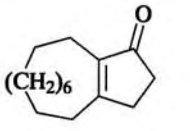
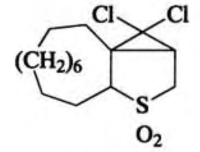
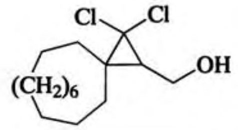
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	80% HOAc, reflux		(70)	112
C_{13} 	TFA, rt, 1.5 h		(72)	110, 109
C_{15} 	TFA, rt, 2.5 h		(90)	110, 109
	80% HOAc, reflux	" (60)		112
	47% HBr, 100°, 2 h	" (37)		111, 109

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS

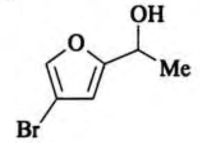
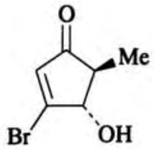
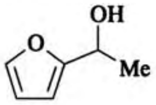
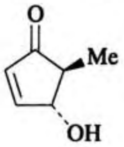
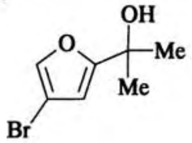
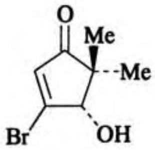
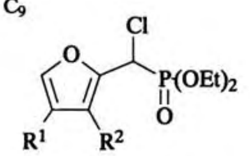
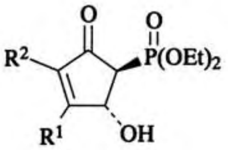
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_6				
	H_2SO_4, H_2O, DME, 85-90°, 6 h		(81)	137
	PPA, 50°, 24 h		(30)	132
C_7				
	H_2SO_4, H_2O, DME, 85-90°, 12 h		(28)	137
C_9				
	DME, H_2O, rt			139
R^1 R^2				
H H		(54)		
Br H		(60)		
H Br		(78)		

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS (*Continued*)

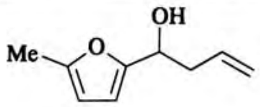
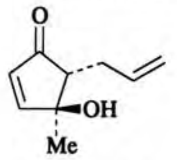
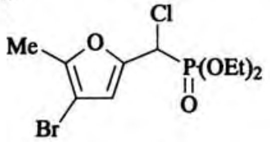
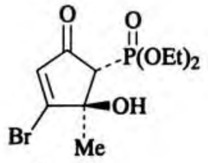
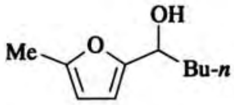
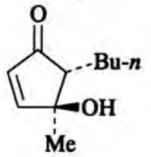
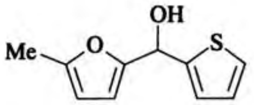
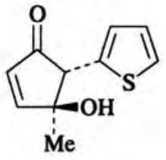
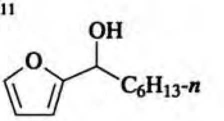
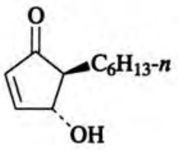
Reactant	Conditions	Product(s) and Yie ld(s) (%)		Refs.
	$ZnCl_2$, H_2O, acetone, 60°, 72 h		(35)	135
C_{10}				
	DME, H_2O, rt		(33)	139
	$ZnCl_2$, H_2O, acetone, 60°, 72 h		(18)	135
	$ZnCl_2$, H_2O, acetone, 60°, 4 h		(85)	135
C_{11}				
	PPA, 50°, 24 h		(70)	132

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS (*Continued*)

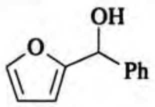
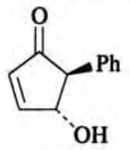
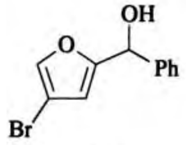
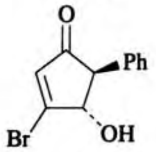
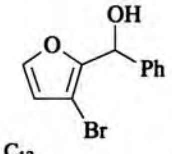
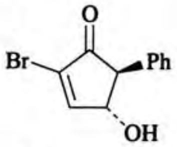
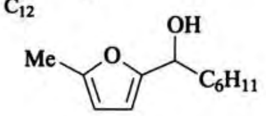
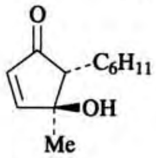
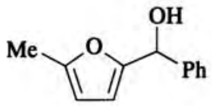
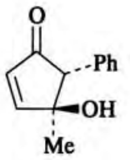
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PPA, 50°, 24 h		(65)	132
	DME, H_2O, H_2SO_4, 85-90°, 1 h		(85)	137
	DME, H_2O, H_2SO_4, 85-90°, 0.3 h		(85)	137
C_{12}				
	$ZnCl_2$, H_2O, acetone, 60°, 72 h		(16)	135
	$ZnCl_2$, H_2O, acetone, 60°, 24 h		(70)	135

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS *(Continued)*

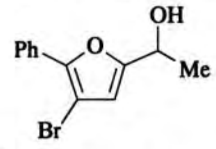
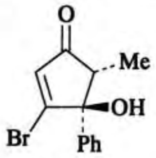
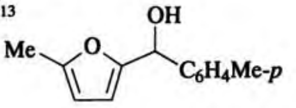
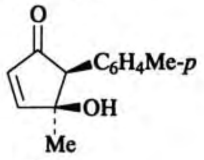
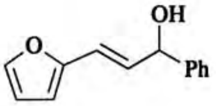
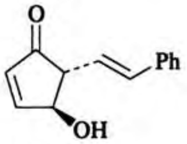
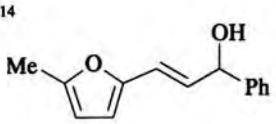
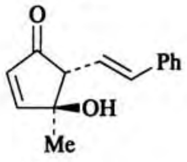
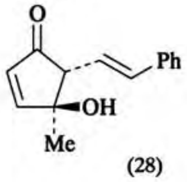
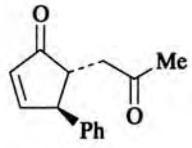
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	DME, H_2O, H_2SO_4, 85-90°, 48 h	 (30)	137
C_{13} 	$ZnCl_2$, H_2O, acetone, 60°, 4 h	 (65)	135
	Acetone, H_2O, 80°, 1.5 h	 (65)	138
C_{14} 	Acetone, H_2O, 70°, 48 h	 (30)	138
	MeCN, H_2O, 55-60°	 +  (28) (2 0)	138

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS *(Continued)*

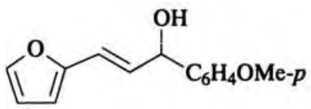
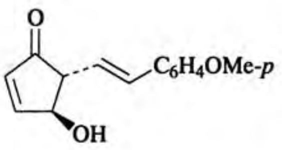
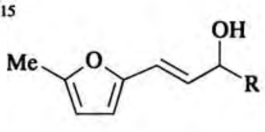
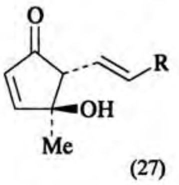
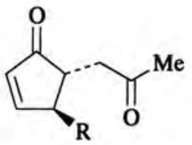
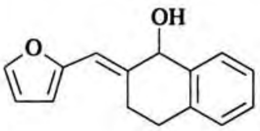
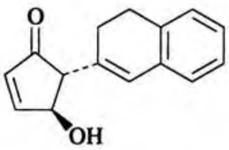
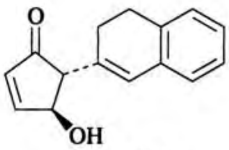
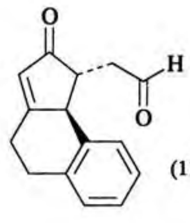
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Acetone, H_2O, 50°, 17 h	 (40)	138
C_{15}  R = C_6H_4Me-*p*	MeCN, H_2O, 55-60°	 +  (27) (20)	138
	Acetone, H_2O, 50°, 48 h	 (43)	138
	MeCN, H_2O, 55-60°	 +  (37) (11)	138

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS *(Continued)*

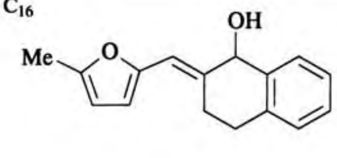
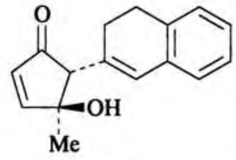
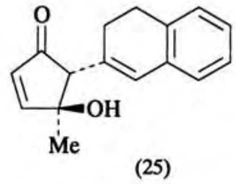
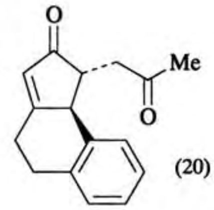
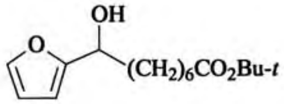
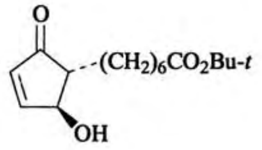
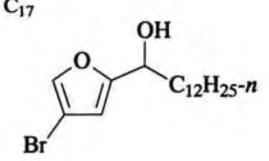
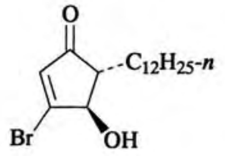
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{16}				
	Acetone, H_2O, 70°, 48 h		(32)	138
	MeCN, H_2O, 55-60°	 (25) +  (20)		138
	PPA, 50°, 24 h		(51)	133
C_{17}				
	DME, H_2O, H_2SO_4, 85-90°, 12 h		(75)	137

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: B. 2-FURYLCARBINOLS *(Continued)*

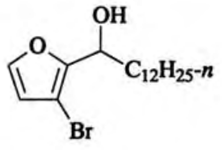
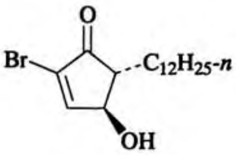
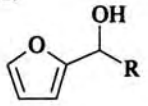
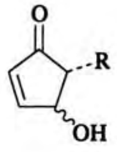
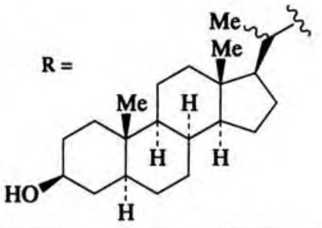
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	DME, H_2O, H_2SO_4, 85-90°, 6 h		(82)	137
C_{26}				
	H_2SO_4, H_2O, acetone, 50°, 30 h		(90)	134
R = 				

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES

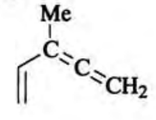
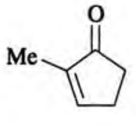
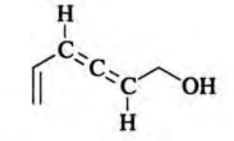
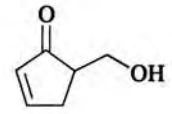
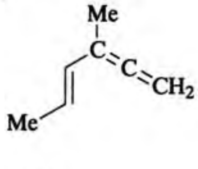
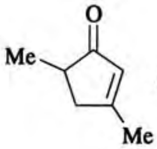
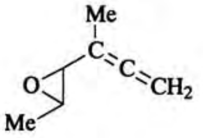
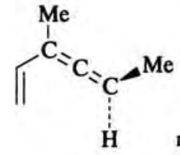
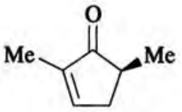
Reactant	Conditions	Pr oduct(s) and Yield(s) (%)	Refs.
C_6			
	PNPBA, CH_2Cl_2, 0°, 24 h	 (60)	114, 113
	$Hg(OAc)_2$, $HClO_4$, HOAc, 25°, 1 h	(31)	127
	t-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt	 (40-70)	125
C_7			
	PNPBA, CH_2Cl_2, 0°, 24 h	 (39) +  (21)	114, 113
 racemic	$Hg(OAc)_2$, $HClO_4$, HOAc, 25°, 1 h	 racemic (20)	127
(*R*)	MCPBA, CH_2Cl_2, 0°, 24 h	(*S*) (—)	116

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

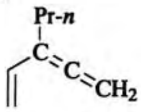
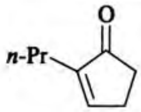
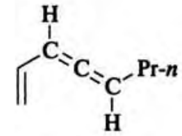
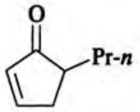
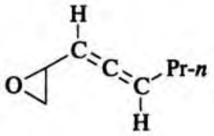
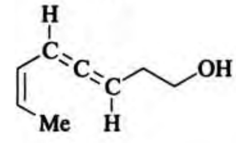
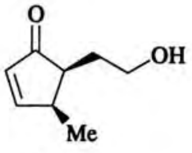
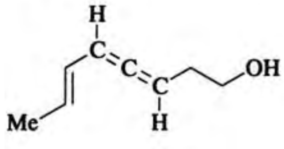
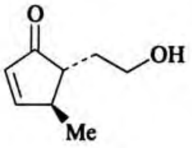
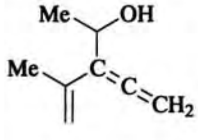
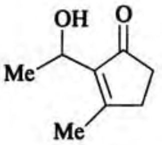
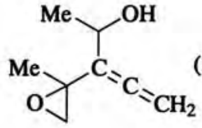
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	PNPBA, CH_2Cl_2, 0°, 24 h	 (60)	114, 113
	PNPBA, CH_2Cl_2, 0°, 24 h	 (57) +  (3)	114, 113
	t-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt	 (40-70)	125
	t-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt	 (40-70)	125
	t-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt	 (65) +  (15)	124

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

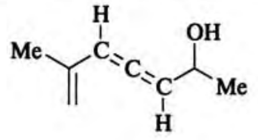
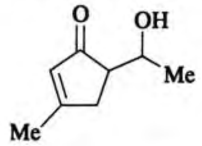
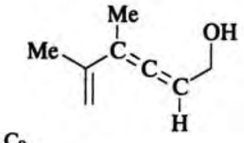
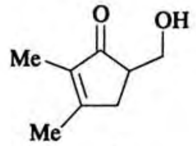
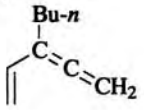
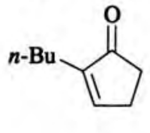
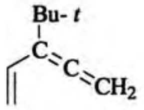
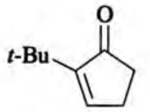
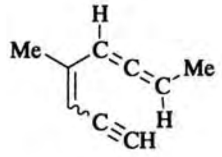
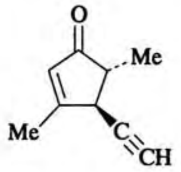
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	t-BuOOH, VO(acac)$_2$, C$_6$H$_6$, 80°, 1.5 h	 (55)	123
	t-BuOOH, VO(acac)$_2$, C$_6$H$_6$, 20°, 1 h; 50°, 3 h	 (50)	123
C$_9$			
	hv, O$_2$, (MeCO)$_2$, CH$_2$Cl$_2$	 (60)	117
	hv, O$_2$, (MeCO)$_2$, CH$_2$Cl$_2$	 (40)	117
	MCPBA, NaHCO$_3$, H$_2$O, 0°, 24 h	 (45)	126

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

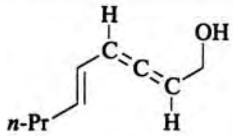
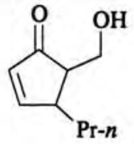
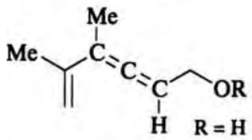
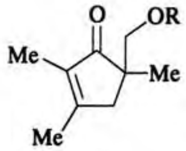
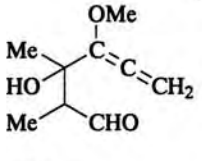
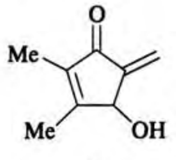
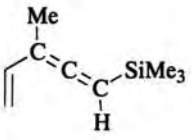
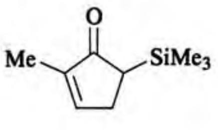
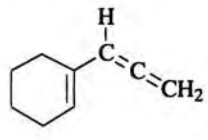
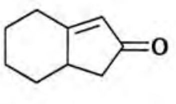
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	t-BuOOH, VO(acac)$_2$, CH$_2$Cl$_2$, rt	 (40-70)	125
 R = H R = Ac	t-BuOOH, VO(acac)$_2$, benzene 20°, 4 h 80°, 4 h	 R = H (45) R = Ac (20)	123
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, -78°, 10 min	 (68)	129
	H$_2$O$_2$, PhCN	 (60)	190
	1. Tl(OAc)$_3$, HOAc, rt 2. HCl, rt, 10 min	 (36)	128

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

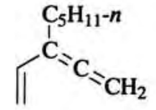
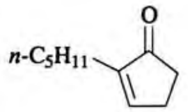
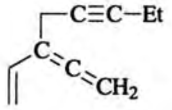
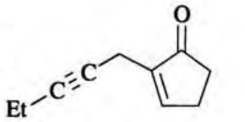
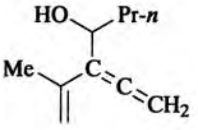
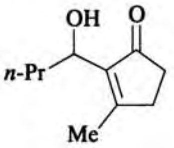
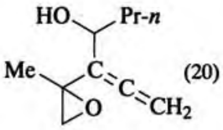
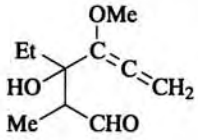
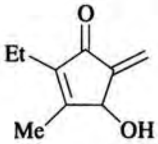
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10}			
			
	PNPBA, CH_2Cl_2, 0°, 24 h	(80)	119
	$Hg(OAc)_2$, $HClO_4$, HOAc, rt, 1 h	(59)	127
	$HClO_4$, 80°, 1 h	(70)	127
	hv, O_2, $(MeCO)_2$, CH_2Cl_2	(55)	117
	1. $Tl(OAc)_3$, HOAc, rt 2. HCl, rt, 10 min	(60)	128
	1. $Hg(OAc)_2$, HOAc, rt, 30 min 2. $HClO_4$, 70°, 1 h	(70)	128
	PNPBA, $NaHCO_3$, CH_2Cl_2, 0°, 24 h	 (45)	120
	*t*-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt, 90 min	 (60) +  (20)	124
	BF_3•OEt_2, CH_2Cl_2, -78°, 10 min	 (72)	129

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

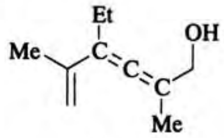
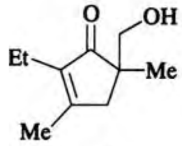
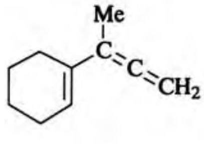
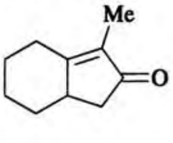
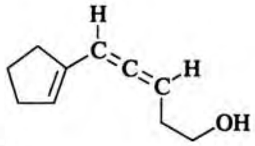
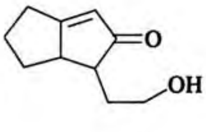
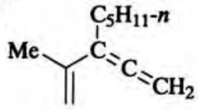
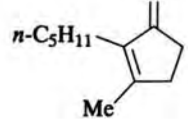
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	*t*-BuOOH, $VO(acac)_2$, C_6H_6, 20°, 4 h	 (63)	123
	1. $Tl(OAc)_3$, HOAc, rt 2. HCl, rt, 10 min	 (60)	128
	1. $Hg(OAc)_2$, HOAc, rt, 30 min 2. $HClO_4$, 70°, 1 h	(75)	128
	*t*-BuOOH, $VO(acac)_2$, CH_2Cl_2, rt	 (40-70)	125
C_{11}			
			
	MCPBA, CH_2Cl_2, 0°, 24 h	(65)	119
	hv, O_2, $(MeCO)_2$, CH_2Cl_2	(35)	117
	1. $Tl(OAc)_3$, HOAc, 40° 2. HCl, rt, 10 min	(45)	128
	1. $Hg(OAc)_2$, HOAc, rt, 30 min 2. $HClO_4$, 70°, 1 h	(54)	128

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

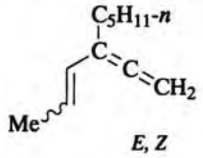
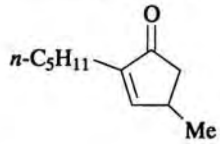
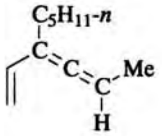
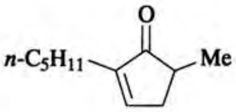
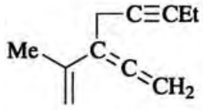
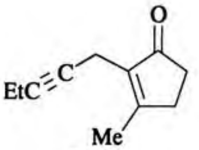
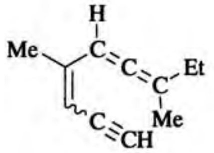
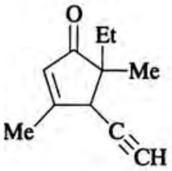
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
 *E, Z*	1. Hg(OAc)$_2$, HOAc, rt, 30 min 2. HClO$_4$, 70°, 1 h		(51)	128
E	"		(78)	128
Z	"		(50)	128
E,Z	1. Tl(OAc)$_3$, HOAc, 40° 2. HCl, rt, 10 min		(25)	128
	Hg(OAc)$_2$, HOAc, HClO$_4$, rt, 1 h		(42)	127
	HClO$_4$, 80°, 1 h		(50)	127
	1. Hg(OAc)$_2$, HOAc, rt, 30 min 2. HClO$_4$, 70°, 1 h		(50)	128
	1. Tl(OAc)$_3$, HOAc, 40° 2. HCl, rt, 10 min		(68)	128
	PNPBA, NaHCO$_3$, CH$_2$Cl$_2$, 0°, 24 h		(70)	120
	MCPBA, NaHCO$_3$, H$_2$O, 0°, 24 h		(58)	126

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

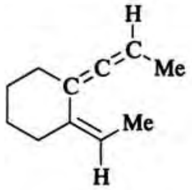
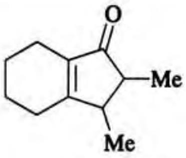
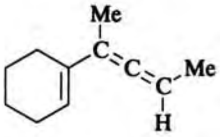
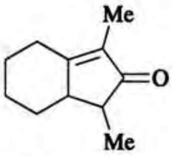
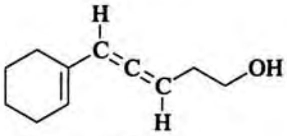
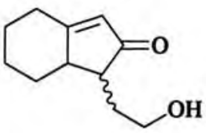
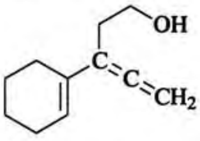
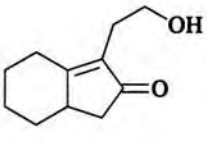
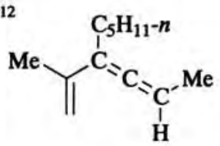
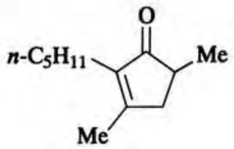
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	PNPBA, CH$_2$Cl$_2$, 0°, 24 h		(50)	118
	PNPBA, CH$_2$Cl$_2$, 0°, 24 h		(50)	118
	1. Hg(OAc)$_2$, HOAc, rt, 30 min 2. HClO$_4$, 70°, 1 h		(49)	128
	1. Tl(OAc)$_3$, HOAc, 40° 2. HCl, rt, 10 min		(44)	128
	*t*-BuOOH, VO(acac)$_2$, CH$_2$Cl$_2$, rt		(40-70)	125
	*t*-BuOOH, VO(acac)$_2$, CH$_2$Cl$_2$, rt		(50)	124
C$_{12}$				
	1. Hg(OAc)$_2$, HOAc, rt, 30 min 2. HClO$_4$, 70°, 1 h		(79)	128
	1. Tl(OAc)$_3$, HOAc, 40° 2. HCl, rt, 10 min		(61)	128

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

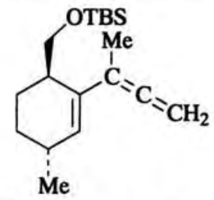
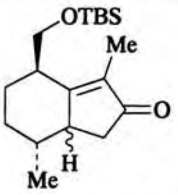
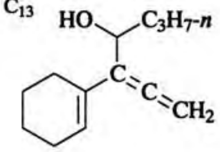
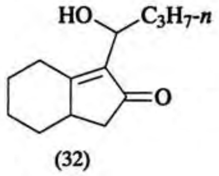
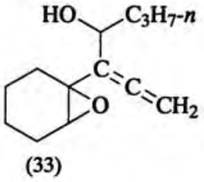
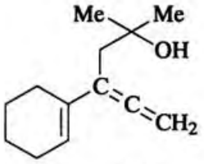
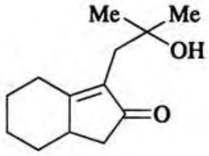
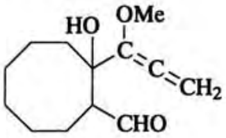
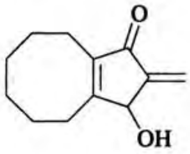
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Tl(OAc)$_3$, HOAc, rt, 30 min	 55:45 (70)	122
C_{13} 	t-BuOOH, VO(acac)$_2$, CH$_2$Cl$_2$, rt	 (32) +  (33)	124
	t-BuOOH, VO(acac)$_2$, CH$_2$Cl$_2$, rt	 (40)	124
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 0°, 10 min	 (80)	129

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

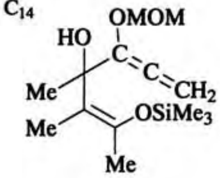
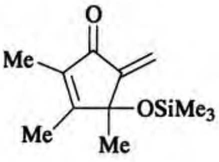
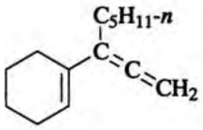
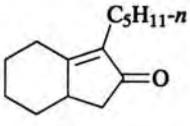
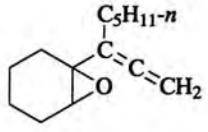
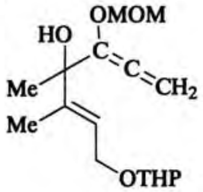
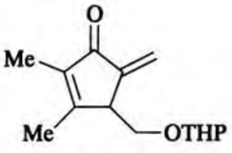
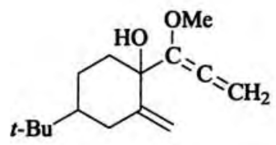
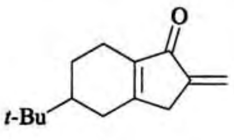
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{14} 	TFAA, 2,6-lutidine, CH$_2$Cl$_2$, -30°	 (83)	191
	hν, O$_2$, (MeCO)$_2$, CH$_2$Cl$_2$	 (40) +  (25)	117
C_{15} 	MeSO$_2$Cl, Et$_3$N, THF, -20 - 0°, 12 h	 (50)	130
	BF$_3$•OEt$_2$, CH$_2$Cl$_2$, 0°, 10 min	 (56)	129

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

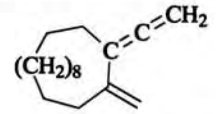
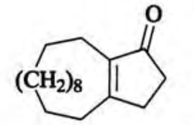
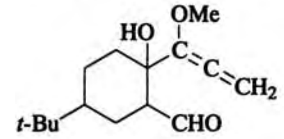
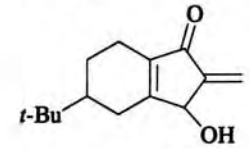
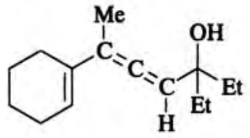
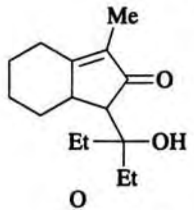
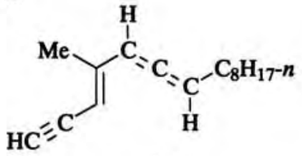
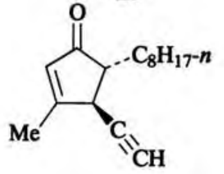
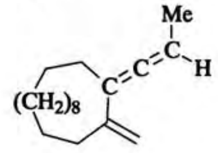
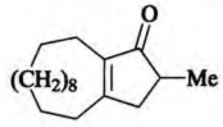
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	MPPA, CH_2Cl_2, Et_2O		(50)	121
	BF_3•OEt_2, CH_2Cl_2, 0°, 10 min		(76)	129
	t-BuOOH, VO(acac)$_2$, C_6H_6, 20°, 1 h		(45)	123
C_{16}				
	MCPBA, CH_2Cl_2, $NaHCO_3$, 0°, 24 h		(58)	126
	MPPA, CH_2Cl_2, Et_2O		(52)	121

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

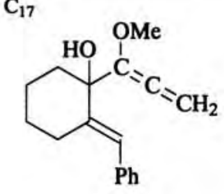
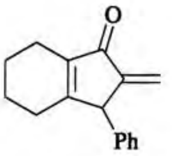
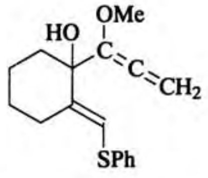
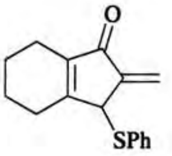
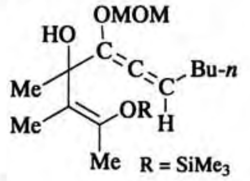
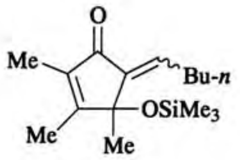
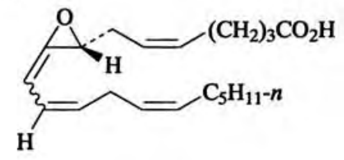
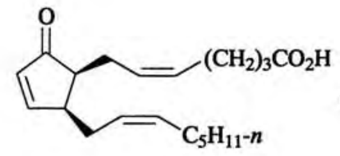
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
C_{17}				
	BF_3•OEt_2, CH_2Cl_2, 0°, 10 min		(78)	129
	BF_3•OEt_2, CH_2Cl_2, 0°, 10 min		(82)	129
C_{18}				
	TFAA, 2,6-lutidine, CH_2Cl_2, -30°		(70)	191
C_{20}				
	rt		(-)	192

TABLE IV. CYCLIZATION OF DIVINYL KETONE EQUIVALENTS FROM SOLVOLYSIS: C. VINYLALLENES (*Continued*)

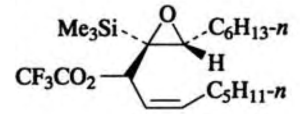
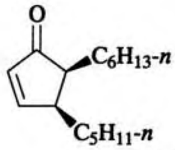
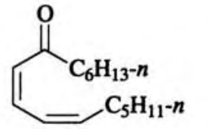
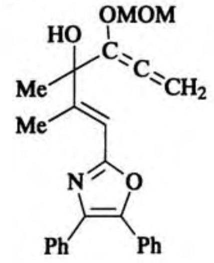
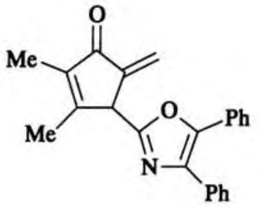
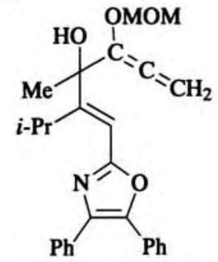
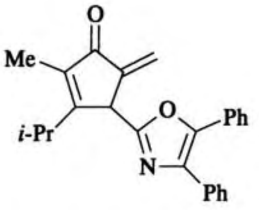
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{21}			
	CsF, MeCN, rt, 10-14 h	 (20-35) +  (20-25)	59
C_{25}			
	TFAA, 2,6-lutidine, CH_2Cl_2, -30°	 (65)	130
C_{27}			
	TFAA, 2,6-lutidine, CH_2Cl_2, -10 to 0°	 (72)	131, 130

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: A. OLEFINIC ACIDS AND ANHYDRIDES

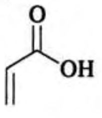
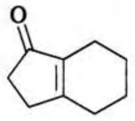
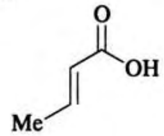
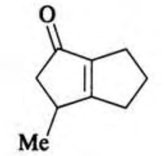
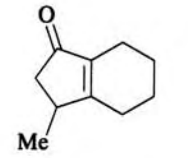
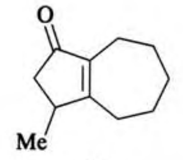
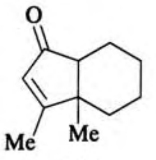
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	Cyclohexene, PPA, 57°, 30 min	 (16)	76
C_4 	Cyclopentene, PPA, 40°, 1 h	 (22)	76
	Cyclohexene, PPA, 40°, 1 h	 (60)	76
	Cycloheptene, PPA, 50°	 (6) +  (18)	174

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: A. OLEFINIC ACIDS AND ANHYDRIDES (*Continued*)

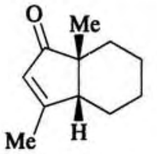
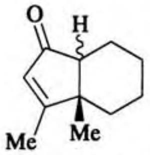
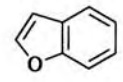
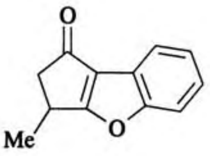
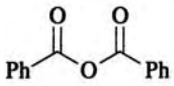
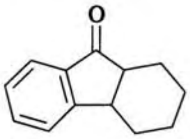
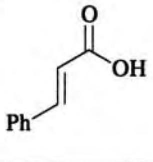
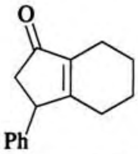
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
		 +		
	Cycloheptene, PPA, 70°	(4)	(29) β:α 62:38	193
	1-Methylcyclohexene, PPA, 70°	(4)	(29) β:α 62:38	193
	 , PPA, 130°		(34)	194
C_7 	Cyclohexene, PPA, 57°, 30 min		(42)	76
C_9 	Cyclohexene, PPA, 57°, 30 min		(26)	76

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: B. OLEFINIC ESTERS

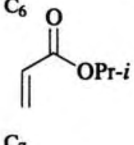
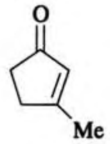
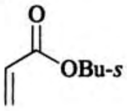
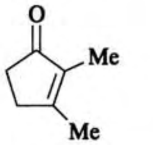
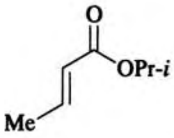
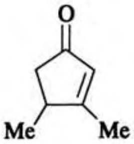
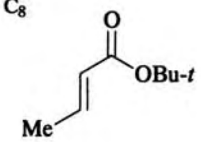
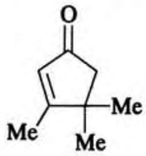
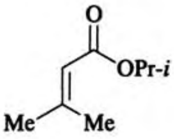
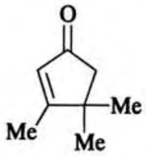
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6 	PPA, 100°, 1 h	 (15-20)	195
C_7 	PPA, 100°, 1h	 (20)	195
	PPA, 100°, 1 h	 (58-67)	195
C_8 	PPA, 100°, 1 h	 (45)	195
	PPA, 100°, 1 h	 (60)	195

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: B. OLEFINIC ESTERS (*Continued*)

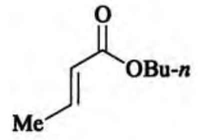
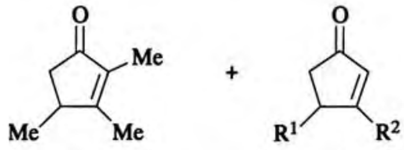
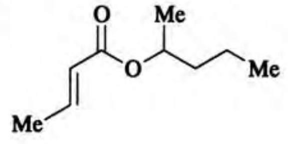
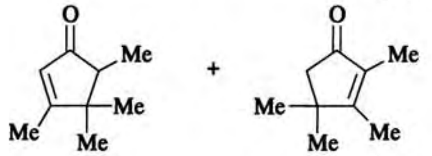
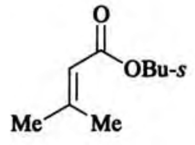
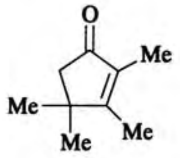
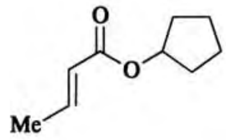
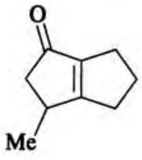
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	PPA, 100°, 12 h	 (6) (4) R^1 = Me or Et R^2 = Et or Me	195
C_9 	PPA, 100°, 7 h	 (36) (9)	195
	PPA, 100°, 1 h	 (60)	195
	PPA, 45-55°, 90 min	 (20)	195

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: B. OLEFINIC ESTERS (*Continued*)

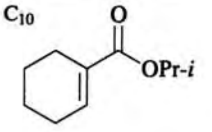
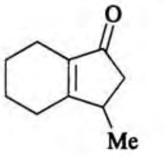
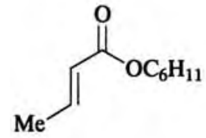
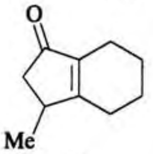
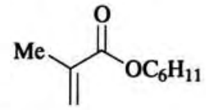
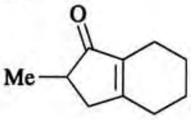
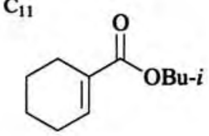
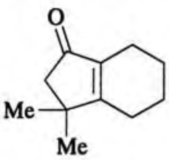
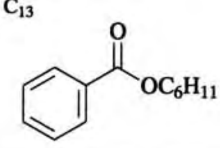
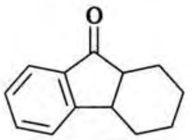
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_{10} 	PPA, 100°, 1 h	 (60)	195
	PPA, 60°, 90 min	 (60)	195
	PPA, 100°, 1 h	 (17)	195
C_{11} 	PPA, 100°, 2 h	 (59)	195
C_{13} 	PPA, 100°, 20 min	 (40)	195

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS

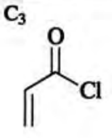
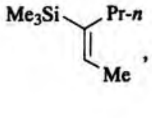
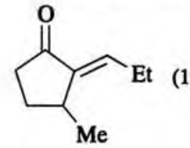
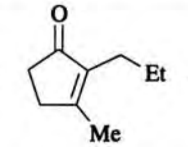
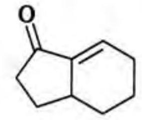
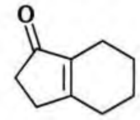
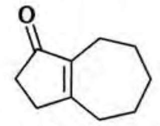
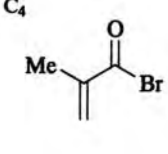
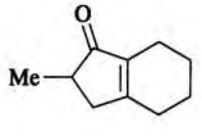
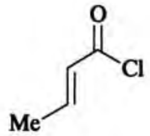
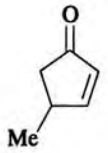
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C$_3$ 	, AlCl$_3$, CH$_2$Cl$_2$, rt, 2 h	 (19) +  (5)	68, 67
	1-Trimethylsilylcyclohexene, AlCl$_3$, CH$_2$Cl$_2$, rt, 2 h	 (15) +  (12)	68, 67
	1. 1-Trimethylsilylcycloheptene, AlCl$_3$, NaOAc, CH$_2$Cl$_2$, -45°, 2 h 2. TFA, rt, 3 h	 (10)	68, 67
C$_4$ 	Cyclohexene, AlCl$_3$, 0°	 (36)	157
	Me$_3$SiCH=CH$_2$, CCl$_4$, 77°, 30 min	 (63)	160

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS (*Continued*)

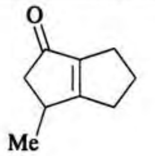
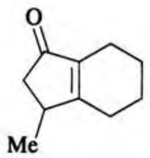
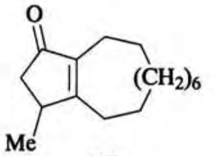
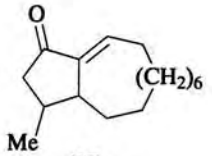
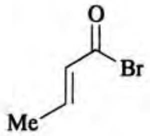
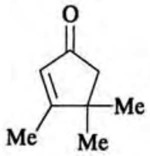
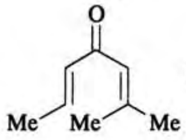
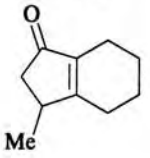
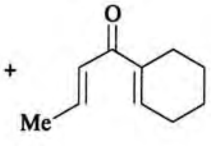
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 1-Trimethylsilylcyclopentene, AlCl$_3$, CH$_2$Cl$_2$, rt, 1 h 2. BF$_3$•OEt$_2$, C$_6$H$_6$, 80°	 (58)	68, 67
	1. 1-Trimethylsilylcyclohexene, AlCl$_3$, CH$_2$Cl$_2$, -78°, 15 min 2. BF$_3$•OEt$_2$, C$_6$H$_6$, 80°, 3 d	 (44)	68, 67
	1. Cyclohexene, AlCl$_3$, CH$_2$Cl$_2$, -10° 2. H$_3$PO$_4$, HCO$_2$H, 80-90°, 4 h	(30)	102
	1. 1-Trimethylsilylcyclododecene, AlCl$_3$, CH$_2$Cl$_2$, rt 2. BF$_3$•OEt$_2$, C$_6$H$_6$, 80°	 (48) +  (18)	68, 67
	MeCH=CMe$_2$, AlCl$_3$, 0°	 (15) +  (50)	157
	Cyclohexene, AlCl$_3$, -78°	 (72) +  (8)	157

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS (*Continued*)

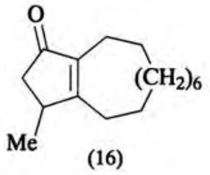
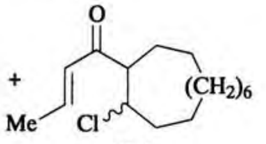
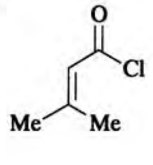
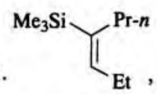
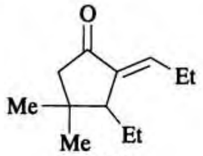
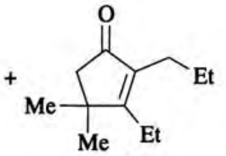
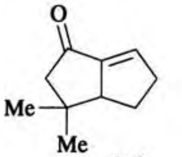
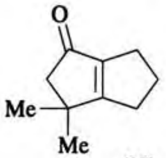
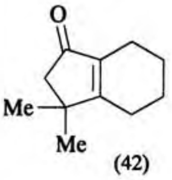
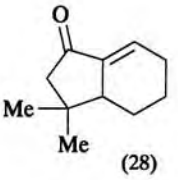
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	cis,trans-Cyclododecene, $AlCl_3$, -78°	 (16) +  (64)	157
C_5 	1.  , $AlCl_3$, CH_2Cl_2, -78° 2. BF_3•OEt_2, C_6H_6, 80°, 1-3 d	 (41) +  (21)	68, 67
	1. 1-Trimethylsilylcyclopentene, $AlCl_3$, -78°, 15 min 2. $SnCl_4$, CH_2Cl_2, reflux, 8-12 h	 (25) +  (37)	68, 67
	1. 1-Trimethylsilylcyclohexene, $AlCl_3$, CH_2Cl_2, -78°, 15 min 2. BF_3•OEt_2, CH_2Cl_2, reflux, 8-12 h	 (42) +  (28)	68, 67

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS (*Continued*)

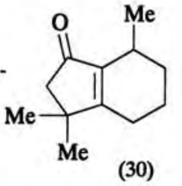
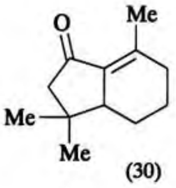
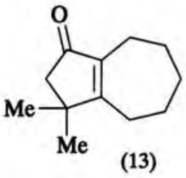
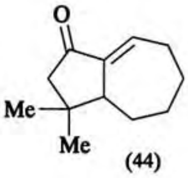
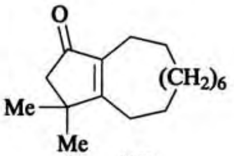
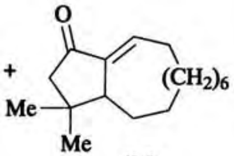
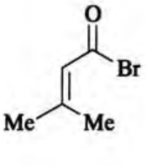
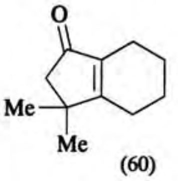
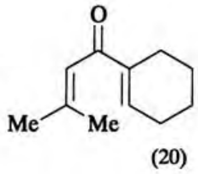
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. 6-Methyl-1-trimethylsilylcyclohexene, $AlCl_3$, CH_2Cl_2, -78°, 15 min 2. BF_3•OEt_2, CH_2Cl_2, reflux, 8-12 h	 (30) +  (30)	68, 67
	1. 1-Trimethylsilylcycloheptene, $AlCl_3$, CH_2Cl_2, -78°, 15 min 2. BF_3•OEt_2, CH_2Cl_2, reflux, 8-12 h	 (13) +  (44)	68, 67
	1. 1-Trimethylsilylcyclododecene, $AlCl_3$, CH_2Cl_2, -78°, 15 min 2. BF_3•OEt_2, C_6H_6, 80°, 1-3 d	 (17) +  (26)	68, 67
	Cyclohexene, $AlCl_3$, -78°	 (60) +  (20)	157

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS *(Continued)*

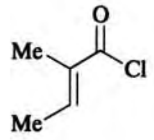
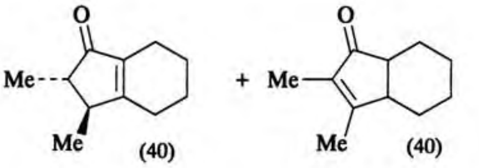
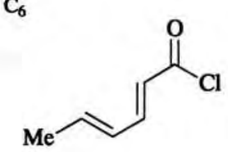
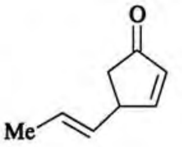
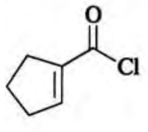
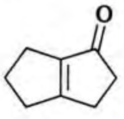
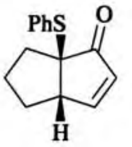
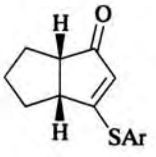
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	Cyclohexene, $AlCl_3$, -78°	 (40) + (40)	157
C_6 	$Me_3SiCH{=}CH_2$, $AlCl_3$, $(CH_2Cl)_2$, 84°, 1 h	 (18-80)	160
	$Me_3SiCH{=}CH_2$, $SnCl_4$, CH_2Cl_2, -30 to 25°, 6 h	 (53)	159, 158
	$Me_3SiCH{=}CHSPh$, $AlCl_3$, $(CH_2Cl)_2$, 80°, 18 h	 (55)	163, 161
	$Me_3Si(ArS)C{=}CH_2$, $AgBF_4$, CH_2Cl_2, $(CH_2Cl)_2$, -50 to 25°, 14-20 h	 Ar = Ph (35-45) Ar = 2,4-$(O_2N)_2C_6H_3$ (58) Ar = 4-ClC_6H_4 (15)	163, 161

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS *(Continued)*

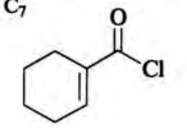
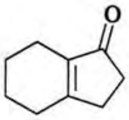
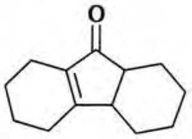
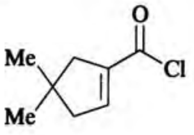
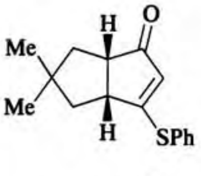
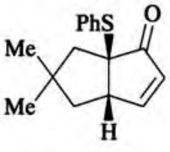
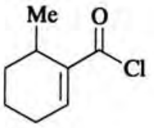
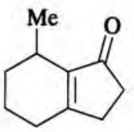
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_7 	$Me_3SiCH{=}CH_2$, $SnCl_4$, CH_2Cl_2, -30 to 25°, 6 h	 (46)	159, 158
	1. Cyclohexene, $AlCl_3$, CH_2Cl_2, -5° 2. H_3PO_4, HCO_2H, 90°, 18 h	 (42)	102
C_8 	$Me_3Si(PhS)C{=}CH_2$, $AgBF_4$, $(CH_2Cl)_2$, -50 to 20°, 20 h	 (38)	163, 161, 162
	$Me_3SiCH{=}CHSPh$, $AlCl_3$, $(CH_2Cl)_2$, 80°, 18 h	 (55)	163, 161
	$Me_3SiCH{=}CH_2$, $SnCl_4$, CH_2Cl_2, -30 to 25°, 6 h	 (64)	159

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: C. OLEFINIC ACID HALIDES AND OLEFINS (*Continued*)

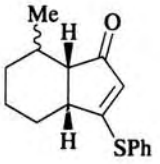
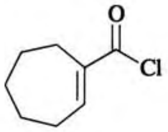
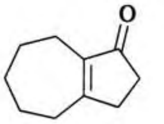
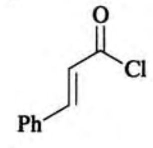
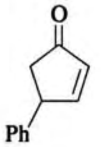
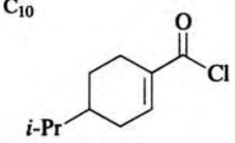
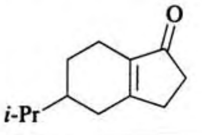
Reactant	Conditions	Product(s) and Yield(s) (%)		Refs.
	$Me_3Si(PhS)C{=}CH_2$, $AgBF_4$, CH_2Cl_2, $(CH_2Cl)_2$, -50 to 20°		(42)	163
	$Me_3SiCH{=}CH_2$, $SnCl_4$, CH_2Cl_2, -30 to 20°, 6 h		(32)	159, 158
C_9				
	$Me_3SiCH{=}CH_2$, $AlCl_3$, CCl_4, 77°, 30 min		(46)	160
C_{10}				
	$Me_3SiCH{=}CH_2$, $SnCl_4$, CH_2Cl_2, -30 to 25°, 6 h		(56)	159, 158

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: D. ACID HALIDES AND PARAFFINS

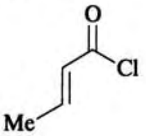
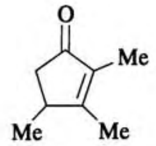
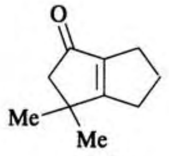
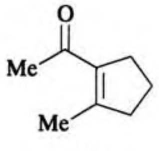
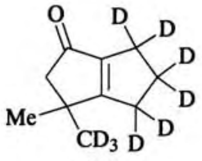
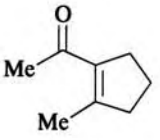
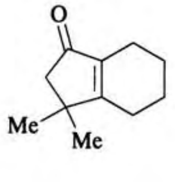
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_4			
	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, reflux, 4 h	 (60)	157a
	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. Methylcyclopentane, AcCl, CH_2Cl_2, reflux, 2 h	 (60) +  (15)	157a
	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. Cyclohexane-d_{12}, AcCl, CH_2Cl_2, reflux, 8 h	 (45) +  (15)	157a
	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. Methylcyclohexane, reflux, 6 h	 (60)	157a

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: D. ACID HALIDES AND PARAFFINS *(Continued)*

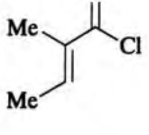
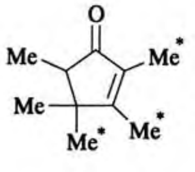
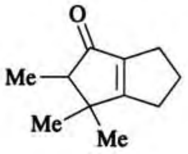
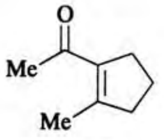
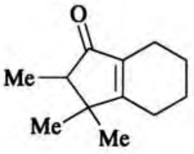
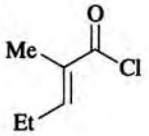
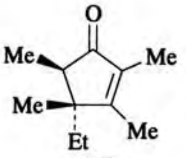
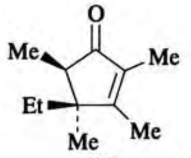
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C5 	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, reflux, 4 h	 * = Me (60)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. $(CD_3)_2CHCH_3$, reflux, 4 h	* = CD_3, (d_6) (60)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. Methylcyclopentane, AcCl reflux, 10 h	 (60) +  (15)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylcyclohexane, reflux, 6 h	 (60)	157a
C6 	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, reflux, 4 h	 (47) +  (14)	157a

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: D. ACID HALIDES AND PARAFFINS *(Continued)*

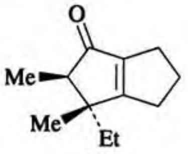
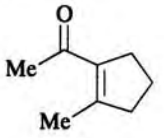
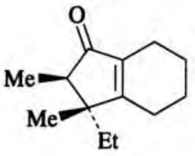
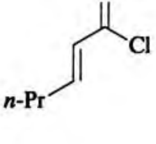
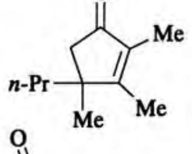
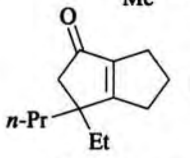
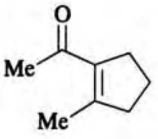
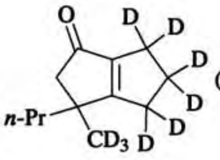
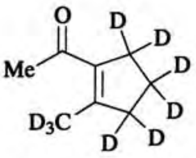
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. Methylcyclopentane, AcCl CH_2Cl_2, reflux, 4 h	 (60) +  (15)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. Methylcyclohexane, CH_2Cl_2, reflux, 4 h	 (60)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, reflux, 4 h	 (60)	157a
	1. AlCl3, $CH_2Cl\ _2$, 0°, 0.5 h 2. Methylcyclopentane, AcCl, CH_2Cl_2, reflux, 5 h	 (60) +  (15)	157a
	1. AlCl3, CH_2Cl_2, 0°, 0.5 h 2. Cyclohexane-d_{12}, AcCl, CH_2Cl_2, reflux, 5 h	 (40) +  (15)	157a

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: D. ACID HALIDES AND PARAFFINS (*Continued*)

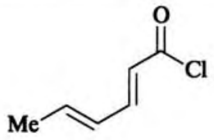
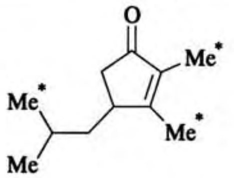
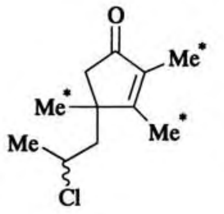
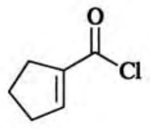
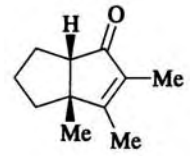
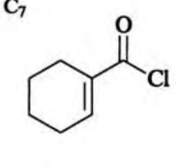
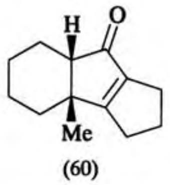
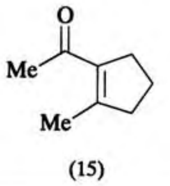
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	1. $AlCl_3$, EtOH, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, rt, 28 h	 * = Me (42)	157a
	1. $AlCl_3$, EtOH, CH_2Cl_2, 0°, 0.5 h 2. $(CD_3)_2CHCH_3$, rt, 28 h	* = CD_3, (d_6) (-)	157a
	1. $AlCl_3$, CH_2Cl_2, $MeNO_2$, H_2O, 0°, 0.25 h 2. 2-Methylbutane, reflux, 3 h	 * = Me (46)	157a
	1. $AlCl_3$, CH_2Cl_2, $MeNO_2$, H_2O, 0°, 0.25 h 2. $(CD_3)_2CHCH_3$, reflux, 3 h	* = CD_3, (d_6) (-)	157a
	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylbutane, reflux, 12 h	 (25)	157a
C_7 	1. $AlCl_3$, CH_2Cl_2, 0°, 0.5 h 2. 2-Methylcyclopentane, AcCl, reflux, 3.5 h	 (60) +  (15)	157a

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES

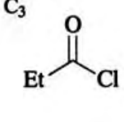
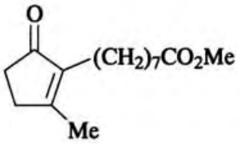
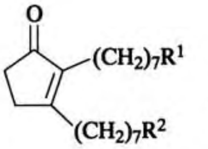
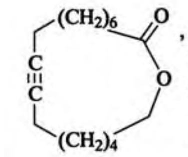
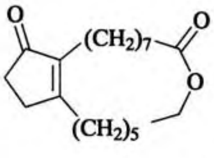
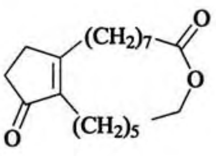
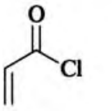
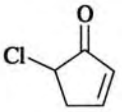
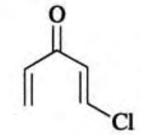
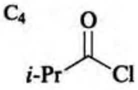
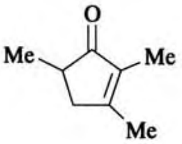
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_3 	MeC≡C$(CH_2)_7CO_2Me$, $AgBF_4$, CH_2Cl_2, -20 to 0°, 10 min	 (35)	170
	$Me(CH_2)_7C≡C(CH_2)_7CO_2Me$, $AgBF_4$, CH_2Cl_2, $(CH_2Cl)_2$, -20 to 0°, 10 min	 R^1 = Me or CO_2Me (15) R^2 = CO_2Me or Me	170
	, $AgBF_4$, CH_2Cl_2, $(CH_2Cl)_2$, -20 to 0°, 10 min	 or  (44)	170
	HC≡CH, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (38) +  (2)	164
C_4 	MeC≡CMe, $AgBF_4$, CH_2Cl_2, $(CH_2Cl)_2$, -60°, 5 min	 (55)	196

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

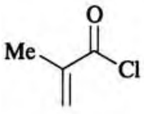
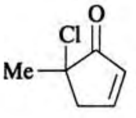
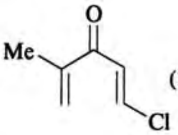
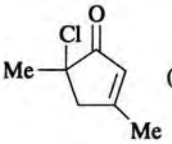
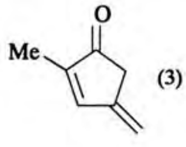
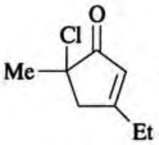
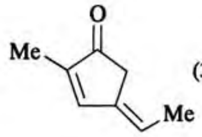
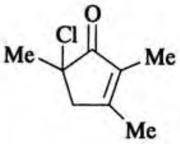
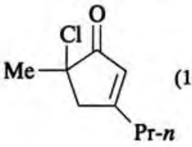
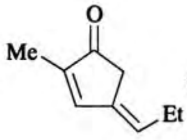
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CH, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (71) +  (1)	164
	HC≡CMe, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (62) +  (3)	166
	HC≡CEt, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (8) +  (33)	166
	MeC≡CMe, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (40)	166
	HC≡CPr-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (10) +  (42)	166

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

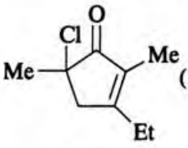
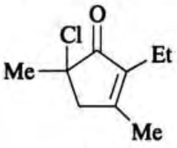
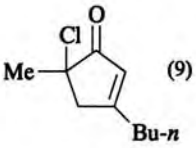
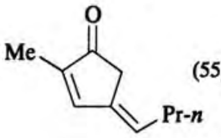
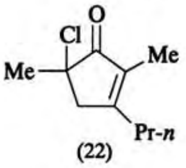
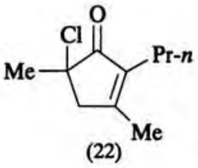
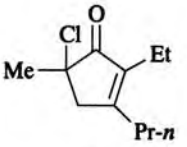
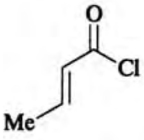
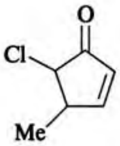
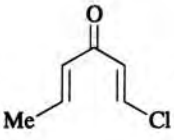
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeC≡CEt, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (17) +  (17)	166
	HC≡CBu-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (9) +  (55)	166
	MeC≡CPr-*n* , $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (22) +  (22)	166
	EtC≡CPr-*n* , $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (55)	166
	HC≡CH, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (53) +  (7)	166

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

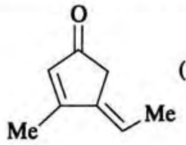
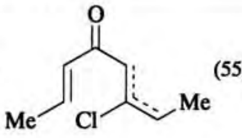
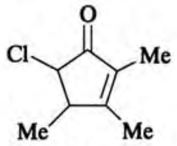
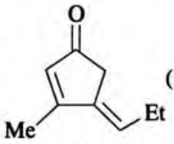
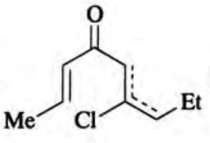
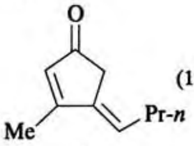
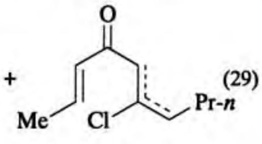
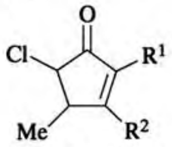
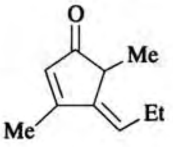
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CEt, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (9) +  (55)	166
	MeC≡CMe, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (30)	166
	HC≡CPr-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (14) +  (31)	166
	HC≡CBu-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (13) +  (29)	166
	MeC≡CPr-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 +  R^1 = Me, R^2 = Pr-*n* ; R^1 = Pr-*n*, R^2 = Me (23) (7)	166

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

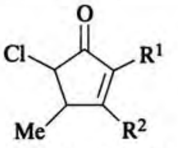
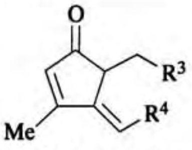
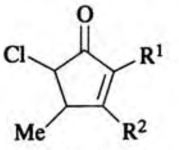
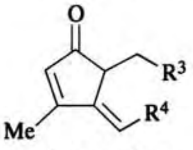
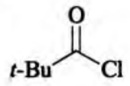
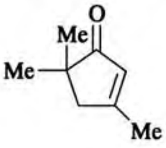
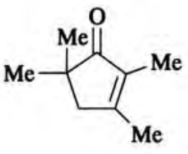
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	MeC≡CBu-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 +  R^1 = Me, R^2 = Bu-*n* ; R^3 = H, R^4 = Pr-*n* ; R^1 = Bu-*n*, R^2 = Me (25) R^3 = Pr-*n*, R^4 = H (5)	166
	EtC≡CPr-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 +  R^1 = Et, R^2 = Pr-*n* ; R^3 = Me, R^4 = Et ; R^1 = Pr-*n*, R^2 = Et (43) R^3 = Et, R^4 = Me (8)	166
C_5 	HC≡CMe, $AgBF_4$, $(CH_2Cl)_2$, -60°, 5 min	 (66)	196
	MeC≡CMe, $AgBF_4$, $(CH_2Cl)_2$, -60°, 5 min	 (73)	196

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

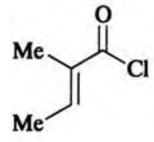
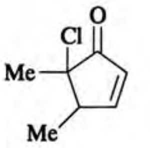
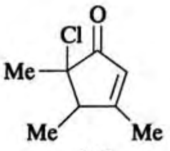
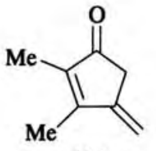
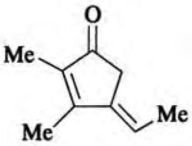
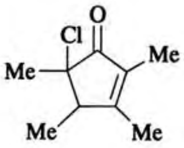
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CH, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (70)	164
	HC≡CMe, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (26) +  (40)	166
	HC≡CEt, Al Cl_3, $(CH_2Cl)_2$, 0-40°, 2 h	 (68)	166
	MeC≡CMe, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (40)	166

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

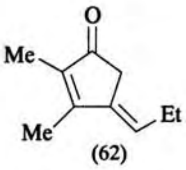
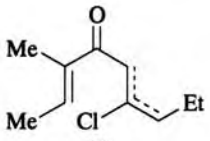
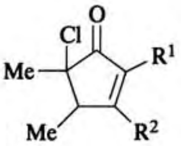
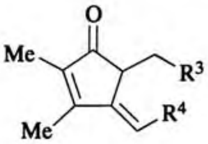
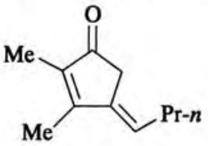
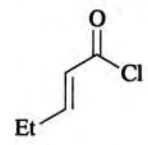
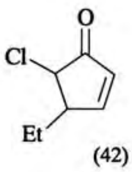
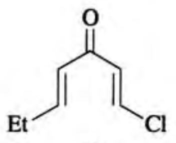
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CPr-*n*, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (62) +  (5)	166
	MeC≡CEt, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 R^1 = Et, R^2 = Me; R^1 =Me, R^2 = Et (54) +  R^3 = H, R^4 = Me ; R^3 = Me, R^4 = H (6)	166
	HC≡CBu-*n*, $AlCl_3$, $(CH_2Cl)_2$, 0-40°, 2 h	 (74)	166
	HC≡CH, $AlCl_3$, $(CH_2Cl)_2$, rt, 6-7 h	 (42) +  (8)	164

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

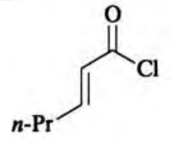
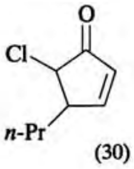
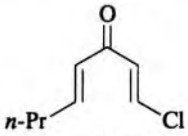
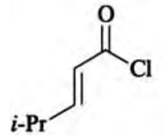
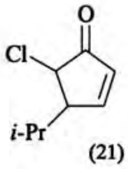
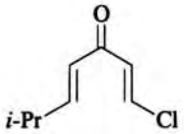
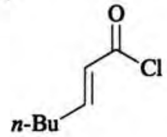
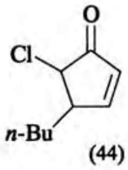
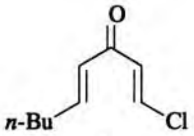
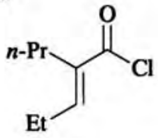
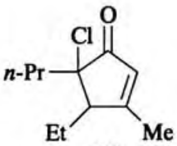
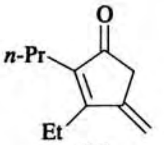
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_6			
	HC≡CH, AlCl$_3$, (CH$_2$Cl)$_2$, rt, 6-7 h	 (30) +  (10)	164
	HC≡CH, AlCl$_3$, (CH$_2$Cl)$_2$, rt, 6-7 h	 (21) +  (9)	164
C_7			
	HC≡CH, AlCl$_3$, (CH$_2$Cl)$_2$, rt, 6-7 h	 (44) +  (2)	164
C_8			
	HC≡CMe, AlCl$_3$, (CH$_2$Cl)$_2$, 0-40°, 2 h	 (16) +  (30)	166

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: E. ACID HALIDES AND ACETYLENES (*Continued*)

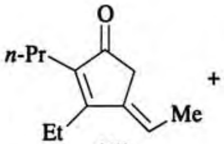
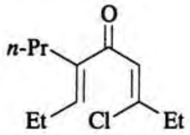
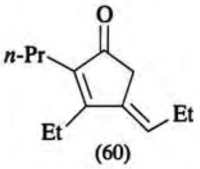
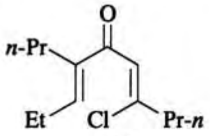
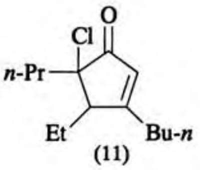
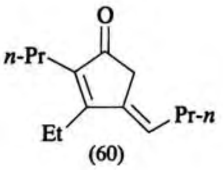
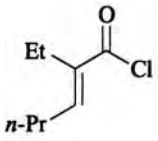
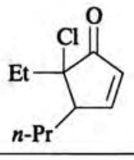
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
	HC≡CEt, AlCl$_3$, (CH$_2$Cl)$_2$, 0-40°, 2 h	 (65) +  (7)	166
	HC≡CPr-*n*, AlCl$_3$, (CH$_2$Cl)$_2$, 0-40°, 2 h	 (60) +  (23)	166
	HC≡CBu-*n*, AlCl$_3$, (CH$_2$Cl)$_2$, 0-40°, 2 h	 (11) +  (60)	166
	HC≡CH, AlCl$_3$, (CH$_2$Cl)$_2$, rt, 6-7 h	 (65)	164

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: F. ORGANOMETALLICS

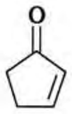
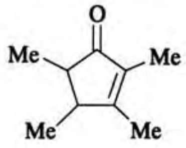
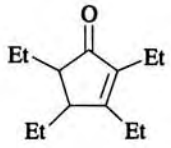
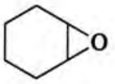
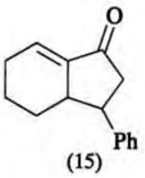
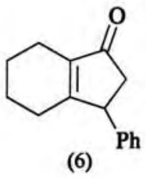
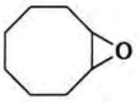
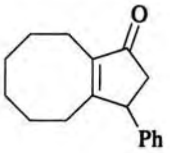
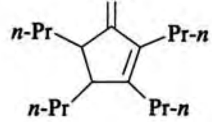
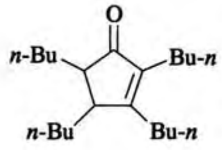
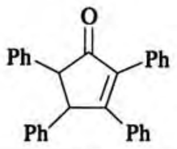
Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_2			
HC≡CH	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60°, 2 h	 (15)	168
C_4			
MeC≡CMe	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60°, 2 h	 (61)	168
C_6			
EtC≡CEt	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60°, 2 h	 (70)	168
	1. Me$_3$SiMn(CO)$_5$,PhC≡CH , Et$_2$O, 1 bar, rt 2. HCO$_2$H, H$_3$PO$_4$, 90°, 2 h	 (15) +  (6)	169

TABLE V. IN SITU CONSTRUCTION OF DIVINYL KETONES: F. ORGANOMETALLICS *(Continued)*

Reactant	Conditions	Product(s) and Yield(s) (%)	Refs.
C_8			
	1. Me$_3$SiMn(CO)$_5$,PhC≡CH , Et$_2$O, 1 bar, rt 2. HCO$_2$H, H$_3$PO$_4$, 90°, 2 h	 (35)	169
n-PrC≡CPr-*n*	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60°, 2 h	 (25)	168
C_{10}			
n-BuC≡CBu-*n*	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60°, 2 h	 (25)	168
C_{14}			
PhC≡CPh	Ni(CO)$_4$, EtOH, HNO$_3$, HCl, 40-60 3, 2 h	 (14)	168

References

1. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1941**, 211 [C.A., **37**, 6243^7 (1943)].
2. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1942**, 200 [C.A., **39**, 1619^4 (1945)].
3. I. N. Nazarov and A. I. Kuznetsova, Izv. Akad. Nauk SSSR, Ser. Khim., **1942**, 392 [C.A., **39**, 1620^3 (1945)].
4. I. N. Nazarov and Ya. M. Yanbikov, Izv. Akad. Nauk SSSR, Ser. Khim., **1943**, 389 [C.A., **39**, 503a (1945)].
5. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1944**, 65 [C.A., **39**, 1620^9 (1945)].
6. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1946**, 529 [C.A., **42**, 7731a (1948)].
7. I. N. Nazarov and L. N. Pinkina, Izv. Akad. Nauk SSSR, Ser. Khim., **1946**, 633 [C.A., **42**, 7731h (1948)].
8. I. N. Nazarov and M. S. Burmistrova, Izv. Akad. Nauk SSSR, Ser. Khim., **1947**, 51 [C.A., **42**, 7732g (1948)].
9. I. N. Nazarov and S. S. Bukhmutskaya, Izv. Akad Nauk SSSR, Ser. Khim., **1947**, 205 [C.A., **42**, 7733e (1948)].
10. I. N. Nazarov and G. P. Verkholetova, Izv. Akad. Nauk SSSR, Ser. Khim., **1947**, 277 [C.A., **42**, 7734a (1948)].
11. I. N. Nazarov and M. S. Burmistrova, Izv. Akad. Nauk SSSR, Ser. Khim., **1947**, 353 [C.A., **42**, 7734i (1948)].
12. I. N. Nazarov and I. I. Zaretskaya, Zh. Obshch. Khim., **18**, 665 (1948) [C.A., **43**, 115f (1949)].
13. I. N. Nazarov and L. N. Pinkina, Zh. Obshch. Khim., **18**, 675 (1948) [C.A., **43**, 116h (1949)].
14. I. N. Nazarov and L. N. Pinkina, Zh. Obshch. Khim., **18**, 681 (1948) [C.A., **43**, 117c (1949)].
15. I. N. Nazarov and I. L. Kotlyarevskii, Zh. Obshch. Khim., **18**, 896 (1948) [C.A., **43**, 117h (1949)].
16. I. N. Nazarov and I. L. Kotlyarevskii, Zh. Obshch. Khim., **18**, 903 (1948) [C.A., **43**, 118d (1949)].
17. I. N. Nazarov and I. L. Kotlyarevskii, Zh. Obshch. Khim., **18**, 911 (1948) [C.A., **43**, 119a (1949)].
18. I. N. Nazarov and S. S. Bakhmutskaya, Zh. Obshch. Khim., **18**, 1077 (1948) [C.A., **43**, 1332g (1949)].
19. I. N. Nazarov and G. P. Verkholetova, Zh. Obshch. Khim., **18**, 1083 (1948) [C.A., **43**, 1333b (1949)].

20. I. N. Nazarov and T. D. Nagibina, Zh. Obshch. Khim., **18**, 1090 (1948) [C.A., **43**, 1333h (1949)].
21. I. N. Nazarov and I. V. Torgov, Zh. Obshch. Khim., **18**, 1338 (1948) [C.A., **43**, 2161h (1949)].
22. I. N. Nazarov and M. S. Burmistrova, J. Gen. Chem. USSR, **20**, 1335 (1950).
23. I. N. Nazarov and I. L. Kotlyarevsky, J. Gen. Chem. USSR, **20**, 1491 (1950).
24. I. N. Nazarov and I. L. Kotlyarevsky, J. Gen. Chem. USSR, **20**, 1501 (1950).
25. I. N. Nazarov and I. L. Kotlyarevsky, J. Gen. Chem. USSR, **20**, 1509 (1950).
26. I. N. Nazarov and S. S. Bakhmutskaya, J. Gen. Chem. USSR, **19**, a223 (1949).
27. I. N. Nazarov and L. N. Pinkina, J. Gen. Chem. USSR, **19**, a331 (1949).
28. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1949**, 178 [C.A., **43**, 6623c (1949)].
29. I. N. Nazarov and I. I. Zaretskaya, Izv. Akad. Nauk SSSR, Ser. Khim., **1949**, 184 [C.A., **43**, 6623h (1949)].
30. I. N. Nazarov and I. L. Kotlyarevskii, Izv. Akad. Nauk SSSR, Ser. Khim., **1949**, 293 [C.A., **43**, 6624f (1949)].
31. I. N. Nazarov and L. N. Pinkina, J. Gen. Chem. USSR, **20**, 2079 (1950).
32. D. N. Kursanov, Z. N. Parnes, I. I. Zaretskaya, and I. N. Nazarov, Izv. Akad. Nauk SSSR, Ser. Khim., **1953**, 114 [C.A., **48**, 3271 (1954)].
33. I. N. Nazarov and M. S. Burmistrova, J. Gen. Chem. USSR, **20**, 2091 (1950).
34. I. N. Nazarov and T. D. Nagibina, J. Gen. Chem. USSR, **23**, 839 (1953).
35. I. N. Nazarov, I. I. Zaretskaya, Z. N. Parnes, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., **1953**, 519 [C.A., **48**, 9930b (1954)].
36. D. N. Kursanov, Z. N. Parness, I. I. Zaretskaya, and I. N. Nazarov, Izv. Akad. Nauk SSSR, Ser. Khim., **1954**, 859 [C.A., **49**, 13910a (1955)].
37. I. N. Nazarov and I. I. Zaretskaya, J. Gen. Chem. USSR, **27**, 693 (1957).
38. I. N. Nazarov, I. I. Zaretskaya, and T. I. Sorkina, J. Gen. Chem. USSR, **30**, 765 (1960).
39. E. A. Braude and J. A. Coles, J. Chem. Soc., **1952**, 1430.
40. D. Vorländer and G. Schroeter, Chem. Ber., **36**, 1490 (1903).
41. C. F. H. Allen, J. A. Van Allen, and J. F. Tinker, J. Org. Chem., **20**, 1387 (1955).
42. F. Francis and F. G. Willson, J. Chem. Soc., **1913**, 2238.
43. C. W. Shoppee and R. E. Lack, J. Chem. Soc., **1969**, 1346.

44. C. W. Shoppee and B. J. A. Cooke, J. Chem. Soc., Perkin Trans. 1, **1973**, 1026.
45. T. S. Sorensen and A. Rauk, in *Pericyclic Reactions*, Vol. **II**, A. P. Marchand and R. E. Lehr, Eds., Academic Press, New York, 1977, pp. 1–67.
46. S. E. Denmark, in *Comprehensive Organic Synthesis*, Vol. **5**, L. A. Paquette, Ed., Pergamon Press, Oxford, 1991, pp. 751–784.
47. C. Santelli-Rouvier and M. Santelli, Synthesis, **1983**, 429.
48. M. Ramaiah, Synthesis, **1984**, 529.
49. M. Ono, J. Syn. Org. Chem. Jpn., **39**, 872 (1981).
50. R. B. Woodward and R. Hoffman, in *The Conservation of Orbital Symmetry*, Verlag Chemie, Weinheim, 1971, pp. 38–64.
51. N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, J. Am. Chem. Soc., **87**, 2153 (1965).
52. T. S. Sorensen, J. Am. Chem. Soc., **89**, 3782 (1967).
53. J. Motoyoshiya, T. Yazaki, and S. Hayashi, J. Org. Chem., **56**, 735 (1991).
54. E. L. Eliel, in *The Stereochemistry of Carbon Compounds*, McGraw Hill, New York, 1960, p. 436.
55. P. H. Campbell, N. W. K. Chiu, K. Deugau, I. J. Miller, and T. S. Sorensen, J. Am. Chem. Soc., **91**, 6404 (1969).
56. N. W. K. Chiu and T. S. Sorensen, Can. J. Chem., **51**, 2776 (1973).
57. R. B. Woodward, Chem. Soc. Special Publication No. 21, 1967, pp. 237–239.
58. C. W. Shoppee and B. J. A. Cooke, J. Chem. Soc., Perkin Trans. 1, **1972**, 2271.
59. E. J. Corey, K. Ritter, M. Yus, and C. Nájera, Tetrahedron Lett., **28**, 3547 (1987).
60. H. Nozaki and M. Kurita, Tetrahedron Lett., **1968**, 3635.
61. R. Noyori, Y. Ohnishi, and M. Katô, J. Am. Chem. Soc., **97**, 928 (1975).
62. C. P. Visser and H. Cerfontain, Recl. Trav. Chim. Pays-Bas, **102**, 307 (1983).
63. D. A. Smith and C. W. Ullmer, III, Tetrahedron Lett., **32**, 725 (1991).
64. D. A. Smith and C. W. Ullmer, III, J. Org. Chem., **56**, 4444 (1991).
65. K. N. Houk, in *Strain and Its Implications In Organic Chemistry*, A. deMeijere and S. Blechert, Eds., Kluwer Academic Publishers, Dodrecht, 1989, pp. 25–37.
66. G. Mehta and N. Krishnamurthy, J. Chem. Soc., Chem. Commun., **1986**, 1319.
67. W. E. Fristad, D. S. Dime, T. R. Bailey, and L. A. Paquette, Tetrahedron

Lett., **1979**, 1999.

68. L. A. Paquette, W. E. Fristad, D. S. Dime, and T. R. Bailey, J. Org. Chem., **45**, 3017 (1980).

69. J. P. Marino and R. J. Linderman, J. Org. Chem., **46**, 3696 (1981).

69a. J. P. F. Andrews and A. C. Regan, Tetrahedron Lett., **32**, 7731 (1991).

70. E. Wada, I. Funiuara, S. Kanemasa, and O. Tsuge, Bull. Chem. Soc. Jpn., **60**, 325 (1987).

71. P. E. Eaton, C. Giordano, G. Schloemer, and U. Vogel, J. Org. Chem., **41**, 2238 (1976).

72. E. A. Braude, W. F. Forbes, and E. A. Evans, J. Chem. Soc., **1953**, 2202.

73. R. E. Lehr, Ph.D. Thesis, Harvard University, 1968.

74. D. B. Kurland, Ph.D. Thesis, Harvard University, 1967.

75. K. E. Harding and K. S. Clement, J. Org. Chem., **49**, 3870 (1984).

76. S. Dev, J. Indian Chem. Soc., **34**, 169 (1957).

77. E. A. Braude and W. F. Forbes, J. Chem. Soc., **1953**, 2208.

78. S. J. de Solms, O. W. Woltersdorf, Jr., E. J. Cragoe, Jr., L. S. Watson, and G. M. Fanelli, Jr., J. Med. Chem., **21**, 437 (1978).

79. S. Hirano, T. Hiyama, and H. Nozaki, Tetrahedron Lett., **1974**, 1429.

80. S. Hirano, S. Takagi, T. Hiyama, and H. Nozaki, Bull. Chem. Soc. Jpn., **53**, 169 (1980).

81. S. E. Denmark and G. A. Hite, Helv. Chim. Acta, **71**, 195 (1988).

82. K. Schaffner and M. Demuth, in *Rearrangements in Ground and Excited States*, Vol. **III**, P. de Mayo, Ed., Academic Press, New York, 1980, p. 281.

82a. A. B. Smith, III and W. C. Agosta, J. Am. Chem. Soc., **95**, 1961 (1973).

82b. L. M. Jackman, E. F. M. Stephenson, and H. C. Yick, Tetrahedron Lett., **1970**, 3325.

83. J. W. Pavlik and L. T. Kavlinkonis, Tetrahedron Lett., **1976**, 1939.

83a. F. G. West, P. V. Fisher, and C. A. Willoughby, J. Org. Chem., **55**, 5936 (1990).

84. S. E. Denmark and T. K. Jones, J. Am. Chem. Soc., **104**, 2642 (1982).

85. T. K. Jones and S. E. Denmark, Helv. Chim. Acta, **66**, 2377 (1983).

86. T. K. Jones and S. E. Denmark, Helv. Chim. Acta, **66**, 2397 (1983).

87. S. E. Denmark, K. L. Habermas, G. A. Hite, and T. K. Jones, Tetrahedron, **42**, 2821 (1986).

88. S. E. Denmark, K. L. Habermas, and G. A. Hite, Helv. Chim. Acta, **71**, 168 (1988).

89. S. E. Denmark and R. C. Klix, Tetrahedron, **44**, 4043 (1988).

90. S. E. Denmark, M. A. Wallace, and C. B. Walker, Jr., J. Org. Chem., **55**, 5543 (1990).
91. J. B. Lambert, G. Wang, R. B. Finzel, and D. H. Teramura, J. Am. Chem. Soc., **109**, 7838 (1987).
92. T. K. Jones and S. E. Denmark, Org. Syn., **64**, 182 (1985).
93. T. K. Jones and S. E. Denmark, J. Org. Chem., **47**, 4595 (1982).
94. R. F. Cunico and F. J. Clayton, J. Org. Chem., **41**, 1480 (1976).
95. G. T. Crisp, W. J. Scott, and J. K. Stille, J. Am. Chem. Soc., **106**, 7500 (1984).
96. I. Fleming, T. W. Newton, and F. Roessler, J. Chem. Soc., Perkin Trans. 1, **1981**, 2527.
97. B. L. Chenard, C. M. Van Zyl, and D. R. Sanderson, Tetrahedron Lett., **27**, 2801 (1986).
98. T. K. Jones, K. L. Habermas, and S. E. Denmark, unpublished results.
99. M. R. Peel and C. R. Johnson, Tetrahedron Lett., **27**, 5947 (1986).
100. M. Franck-Neumann, M. Miesch, and E. Lacroix, Tetrahedron Lett., **30**, 3533 (1989).
100a. M. Franck-Neumann, M. Miesch, and L. Gross, Tetrahedron Lett., **33**, 3879 (1992).
101. R. M. Jacobson, G. P. Lahm, and J. W. Clader, J. Org. Chem., **45**, 395 (1980).
102. G. Baddeley, H. T. Taylor, and W. Pickles, J. Chem. Soc., **1953**, 124.
103. N. Jones and H. T. Taylor, J. Chem. Soc., **1959**, 4017.
104. R. Jacquier, M. Mousseron, and S. Boyer, Bull. Soc. Chim. Fr., **1956**, 1653.
105. T. Sakai, K. Miyata, and A. Takeda, Chem. Lett., **1985**, 1137.
106. D. A. Jackson, M. Rey, and A. S. Dreiding, Helv. Chim. Acta, **66**, 2330 (1983).
107. D. A. Jackson, M. Rey, and A. S. Dreiding, Helv. Chim. Acta, **68**, 439 (1985).
108. D. A. Jackson, M. Rey, and A. S. Dreiding, Tetrahedron Lett., **24**, 4817 (1983).
109. T. Hiyama, M. Shinoda, M. Tsukanaka, and H. Nozaki, Bull. Chem. Soc. Jpn., **53**, 1010 (1980).
110. T. Hiyama, M. Shinoda, and H. Nozaki, Tetrahedron Lett., **1978**, 771.
111. T. Hiyama, M. Tsukanaka, and H. Nozaki, J. Am. Chem. Soc., **96**, 3713 (1974).
112. Y. Gaoni, Tetrahedron Lett., **1978**, 3277.
113. J. Grimaldi and M. Bertrand, Bull. Soc. Chim. Fr., **1971**, 957.

114. J. Grimaldi and M. Bertrand, Tetrahedron Lett., **1969**, 3269.
115. W. Smadja, Chem. Rev., **83**, 263 (1983).
116. M. Bertrand, J. P. Dulcere, and G. Gil, Tetrahedron Lett., **1977**, 4403.
117. M. Malacria and J. Goré, J. Org. Chem., **44**, 885 (1979).
118. M. Bertrand, J.-P. Dulcère, J. Grimaldi, and M. Malacria, C. R. Seances Acad. Sci., Ser. C, **279**, 805 (1974).
119. M. L. Roumestant, M. Malacria, and J. Goré, Synthesis, **1976**, 755.
120. M. Malacria and M. L. Roumestant, Tetrahedron, **33**, 2813 (1977).
121. M. Bertrand, J. P. Dulcere, G. Gil, and M. L. Roumestant, Tetrahedron Lett., **1979**, 1845.
122. R. Baudouy, J. Sartoretti, and F. Choplin, Tetrahedron, **39**, 3293 (1983).
123. A. Doutheau, J. Sartoretti, and J. Goré, Tetrahedron, **39**, 3059 (1983).
124. A. Doutheau, J. Goré, and J. Diab, Tetrahedron, **41**, 329 (1985).
125. S. J. Kim and J. K. Cha, Tetrahedron Lett., **29**, 5613 (1988).
126. A. Doutheau, J. Goré, and M. Malacria, Tetrahedron, **33**, 2393 (1977).
127. F. Delbecq and J. Goré, Tetrahedron Lett., **1976**, 3459.
128. R. Baudouy, F. Delbecq, and J. Goré, Tetrahedron, **36**, 189 (1980).
129. M. A. Tius and D. P. Astrab, Tetrahedron Lett., **25**, 1539 (1984).
130. M. A. Tius, D. P. Astrab, A. H. Fauq, J. B. Ousset, and S. Trehan, J. Am. Chem. Soc., **108**, 3438 (1986).
131. M. A. Tius and D. P. Astrab, Tetrahedron Lett., **30**, 2333 (1989).
132. G. Piancatelli, A. Scettri, and S. Barbadoro, Tetrahedron Lett., **1976**, 3555.
133. G. Piancatelli and A. Scettri, Tetrahedron Lett., **1977**, 1131.
134. G. Piancatelli and A. Scettri, Tetrahedron, **33**, 69 (1977).
135. G. Piancatelli, A. Scettri, G. David, and M. D'Auria, Tetrahedron, **34**, 2775 (1978).
136. G. Piancatelli, Heterocycles, **19**, 1735 (1982).
137. M. D'Auria, F. D'Onofrio, G. Piancatelli, and A. Scettri, Gazz. Chim. Ital., **116**, 173 (1986).
138. R. Antonioletti, A. De Mico, G. Piancatelli, A. Scettri, and O. Ursini, Gazz. Chim. Ital., **116**, 745 (1986).
139. E. Castagnino, M. D'Auria, A. De Mico, F. D'Onofrio, and G. Piancatelli, J. Chem. Soc., Chem. Commun., **1987**, 907.
140. L. I. Zakharkin, A. P. Pryanishnikov, and V. V. Guseva, J. Org. Chem. USSR, **18**, 80 (1981).
141. T. Mandai, T. Yanagi, K. Araki, Y. Morisaki, M. Kawada, and J. Otera, J. Am. Chem. Soc., **106**, 3670 (1984).
142. V. Rautenstrauch, J. Org. Chem., **49**, 950 (1984).

143. P. E. Eaton, A. Srikrishna, and F. Uggeri, J. Org. Chem., **49**, 1728 (1984).
144. P. E. Eaton, R. H. Müller, G. R. Carlson, D. A. Cullison, G. F. Cooper, T.-C. Chou, and E. P. Krebs, J. Am. Chem. Soc., **99**, 2751 (1977).
145. G. A. MacAlpine, R. A. Raphael, A. Shaw, A. W. Taylor, and H.-J. Wild, J. Chem. Soc., Perkin Trans. 1, **1976**, 410.
146. M. A. MacKervey, P. Vibuljan, G. Ferguson, and P. Y. Siew, J. Chem. Soc., Chem. Commun., **1981**, 912.
147. T. Hiyama, M. Shinoda, H. Saimoto, and H. Nozaki, Bull. Chem. Soc. Jpn., **54**, 2747 (1981).
148. L. A. Paquette and A. Leone-Bay, J. Am. Chem. Soc., **105**, 7352 (1983).
149. T. Hiyama, M. Shinoda, and H. Nozaki, J. Am. Chem. Soc., **101**, 1599 (1979).
150. Y. Arai, K. Takeda, K. Masuda, and T. Koizumi, Chem. Lett., **1985**, 1531.
151. J. G. Witteveen and A. J. A. van der Weerdt, Recl. Trav. Chim. Pays-Bas, **100**, 383 (1981).
152. M. Baumann, W. Hoffmann, and N. Müller, Tetrahedron Lett., **1976**, 3585.
153. H. Saimoto, T. Hiyama, and H. Nozaki, Tetrahedron Lett., **21**, 3897 (1980).
154. L. I. Zakharkin, A. P. Pryanishikov, and V. V. Guseva, J. Org. Chem. USSR, **18**, 83 (1981).
155. A. M. Islam and R. A. Raphael, J. Chem. Soc., **1953**, 2247.
156. D. R. Williams, A. Abbaspour, and R. M. Jacobson, Tetrahedron Lett., **22**, 3565 (1981).
157. S. Hacini, R. Pardo, and M. Santelli, Tetrahedron Lett., **1979**, 4553.
157a. C. Morel-Fourrier, J.-P. Dulcère, and M. Santelli, J. Am. Chem. Soc., **113**, 8062 (1991).
158. F. Cooke, J. Schwindeman, and P. Magnus, Tetrahedron Lett., **1979**, 1995.
159. F. Cooke, R. Moerck, J. Schwindeman, and P. Magnus, J. Org. Chem., **45**, 1046 (1980).
160. G. Kjeldsen, J. S. Knudsen, L. S. Ravn-Petersen, and K. B. G. Torssell, Tetrahedron, **39**, 2237 (1983).
161. P. Magnus, D. A. Quagliato, and J. C. Huffman, Organometallics, **1**, 1240 (1982).
162. P. Magnus and D. A. Quagliato, Organometallics, **1**, 1243 (1982).
163. P. Magnus and D. Quagliato, J. Org. Chem., **50**, 1621 (1985).
164. G. J. Martin and G. Daviaud, Bull. Soc. Chim. Fr., **1970**, 3098.

165. G. J. Martin, C. Rabiller, and G. Mabon, Tetrahedron Lett., **1970**, 3131.
166. G. J. Martin, C. Rabiller, and G. Mabon, Tetrahedron, **28**, 4027 (1972).
167. C. Rabiller, G. Mabon, and G. J. Martin, Bull. Chim. Soc. Fr., **1973**, 3462.
168. W. Best, B. Fell, and G. Schmidt, Chem. Ber., **109**, 2914 (1976).
[illegible]
169. P. R. DeShong and D. R. Sidler, J. Org. Chem., **53**, 4892 (1988).
170. K. S. Jadhav, S. B. Thakur, and S. C. Bhattacharyya, Indian J. Chem., **16B**, 280 (1978).
171. H. Schostarez and L. A. Paquette, Tetrahedron, **37**, 4431 (1981).
172. W. Oppolzer and K. Bättig, Helv. Chim. Acta, **64**, 2489 (1981).
173. M. Horton and G. Pattenden, J. Chem. Soc., Perkin Trans. 1, **1984**, 811.
173a. K. F. Cheng, K.-P. Chan, and T.-F. Lai, J. Chem. Soc., Perkin Trans. 1, **1991**, 2461.
174. L. Rand and R. J. Dolinski, J. Org. Chem., **31**, 3063 (1966).
175. B. A. Vick and D. C. Zimmerman, Biochem. Biophys. Res. Commun., **111**, 470 (1983).
176. M. Hamberg, Biochim. Biophys. Acta, **920**, 76 (1987).
177. E. J. Corey, M. d'Alarcao, S. P. T. Matsuda, P. T. Lansbury, Jr., and Y. Yamada, J. Am. Chem. Soc., **109**, 289 (1987).
178. T. M. Harris, S. W. Baertschi, and A. R. Brash, J. Am. Chem. Soc., **111**, 5003 (1989).
179. L. A. Paquette and K. E. Stevens, Can. J. Chem., **62**, 2415 (1984).
180. K. E. Stevens and L. A. Paquette, Tetrahedron Lett., **22**, 4393 (1981).
181.

182. J. A. Barltrop, A. C. Day, and C. J. Samuel, J. Chem. Soc., Chem. Commun., **1977**, 598.
183. R. Noyori, Y. Ohnishi, and M. Kato, J. Am. Chem. Soc., **94**, 5105 (1972).
184. S. E. Denmark and E. M. Carreira, unpublished results.
185. L. A. Paquette and H.-J. Kang, J. Am. Chem. Soc., **113**, 2610 (1991).
186. R. M. Jacobson and G. P. Lahm, J. Org. Chem., **44**, 462 (1979).
187. J. C. Hamlet, H. B. Henbest, and E. R. H. Jones, J. Chem. Soc., **1951**, 2652.
188. T. Hiyama, M. Shinoda, and H. Nozaki, Tetrahedron Lett., **1979**, 3529.
189. Y. Gaoni, Tetrahedron Lett., **1977**, 371.
190. J.-P. Dulcere, J. Grimaldi, and M. Santelli, Tetrahedron Lett., **22**, 3179 (1981).
191. M. A. Tius and X.-M. Zhou, Tetrahedron Lett., **30**, 4629 (1989).
192. A. R. Brash, J. Am. Chem. Soc., **111**, 1891 (1989).

193. S. B. Kulkarni and S. Dev, Tetrahedron, **24**, 545 (1968).
194. H. G. Grant, J. Heterocyclic Chem., **15**, 1235 (1978).
195. J.-M. Conia and M.-L. Leriverend, Bull. Soc. Chim. Fr., **1970**, 2981.
196. A. A. Schegolev, W. A. Smit, G. V. Roitburd, and V. F. Kucherov, Tetrahedron Lett., **1974**, 3373.